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USE OF MONTE-CARLO SIMULATIONS IN POLYURETHANE POLYMERIZATION PROCESSES

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USE OF MONTE-CARLO SIMULATIONS  
IN POLYURETHANE POLYMERIZATION PROCESSES

by

C. Dubois

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Approved by/approuvé par

 1.11.95

Director/Directeur

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Date

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### ABSTRACT

The processing of thermoset energetic polymers involves processes in which a polymerization of an initial liquid prepolymer takes place. This chemical reaction results in a significant increase of the molecular weight of the polymer. Consequently, the rheological properties of the material are also affected by this curing phenomenon. The extent of this reaction, as well as the type of polymer used, often determine the magnitude of these changes and their effect on the quality of the end-product being processed. In order to optimize the processing window of polyurethane-based formulations, the polymerization reaction has been modeled by Monte-Carlo simulations. For this purpose, a numerical code has been developed in ANSI Fortran 77 that allows the simulation of  $A_2+B_2$  polymerization with provision for unequal reactivity of the reaction sites. Simulations have been carried out on HTPB-TDI, PPG-HDI and GAP-IPDI systems. A limited experimental validation has confirmed the validity of the molecular weight distributions calculated by the numerical code. The information obtained from these simulations should provide a means to estimate the material functions of the polymer during the mixing and casting of a formulation by transforming the molecular weight distribution into a relaxation time distribution. Minor modifications to the algorithm will enable the simulation of more complex  $A_n+B_n$  systems.

### RÉSUMÉ

La mise en oeuvre de polymères énergétiques thermodurcissables implique des opérations comprenant la polymérisation d'un prépolymère liquide. Cette réaction chimique se traduit par une augmentation importante de la masse molaire du polymère. En conséquence, les propriétés rhéologiques du matériel sont elles aussi très affectées par le phénomène de cuisson. L'avancement de la réaction, ainsi que le type de polymère utilisé, déterminent souvent l'importance de ces changements et leur effet sur la qualité des produits finis. Afin d'optimiser les conditions d'opérations pour la mise en oeuvre de compositions à base de polyuréthane, la réaction de polymérisation a été modélisée par des simulations numériques stochastiques. A cet effet, un code a été développé en Fortran 77 selon la norme ANSI. Ce programme permet la simulation de systèmes de type  $A_2+B_2$  avec la possibilité de prendre en considération la différence de réactivité entre les sites. Des simulations ont été effectuées pour les systèmes réactifs HTPB-TDI, PPG-HDI et GAP-IPDI. Des travaux expérimentaux ont permis de valider les résultats de distribution des masses molaires obtenus par le logiciel de simulation. Il appert que l'information obtenue permettrait d'estimer les fonctions matérielles du polymère durant le malaxage et la coulée d'une composition en transformant la distribution des masses molaires en distribution des temps de relaxation. Des modifications mineures devront être apportées au code afin de permettre la simulation de systèmes plus complexes de type  $A_n+B_n$ .



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## EXECUTIVE SUMMARY

In times of constant reduction of spending for defence purposes, military industries are challenged to produce state-of-the-art weapons and ammunition at the lowest cost possible. Hence, any technology transferred from CRAD to industry must be developed in keeping in mind these economic considerations. Accordingly, research and development in explosives and propellants must be carried out in such a way that new formulations can be easily produced by Canadian industry. For thermoset composite materials, the knowledge of the rheology of a formulation is critical information in the establishment of a processing window for mixing and casting operations.

Recent advances in polymer rheology have demonstrated the possibility of estimating most of the material functions from the molecular weight distribution (MWD) of the polymer. Unfortunately, the molecular weight distribution of thermoset polymers changes continuously over the processing cycle, starting from the moment that the curing agent is added to the formulation. In a first step toward a predictive model for explosive and propellant production processes, this memorandum reports the use of a stochastic algorithm to describe quantitatively the evolution of molecular species during polyurethane formation. A computer code was developed to carry out this algorithm. Simulations on simplified formulations based on hydroxy-terminated polybutadiene (HTPB) and glycidyl azide polymer (GAP) have been performed. The molecular weight distributions obtained have been verified by gel permeation chromatography experiments. From these results, it appears that the software would be able to predict the molecular weight distribution of most polyurethane formulations before gel point.

Since a significant linkage exists between the rheology of the polymer and its predicted molecular structure, the Monte-Carlo simulations would be a very useful tool for the development of new propellant formulations. By simulating the processing of new thermoset polymers, the cost of their development would be reduced and more ingredient combinations could be tested in the same amount of time. Also, formulations that could not be processed into a defect-free end-product would be discarded from the start. Hence, more complex energetic materials will be developed and this will benefit to the Canadian Armed Forces by making available to them more powerful weapon systems, at a better cost.



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a	exponent for $\eta_0$ - M relation
F	frequency factor for reaction event
F(M,t)	relaxation time function
G(t)	relaxation time spectrum
G <sub>N</sub>	plateau modulus
G'	storage modulus
G''	loss modulus
GPC	gel permeation chromatography
HDI	1,2 diisocyanatohexane
HTPB	hydroxy terminated polybutadiene
IPDI	isophoronediiisocyanate
K	constant
k <sub>i</sub>	rate constant
LWV	link weight vector
M	molecular weight of a single species (or monodisperse polymer)
M <sub>0</sub>	total amount of polymer (mass)
M <sub>e</sub>	minimum molecular weight for entanglement
m <sub>i</sub>	mass fraction of a species within a polymer
M <sub>i</sub>	molecular weight of a species within a polymer
M <sub>n</sub>	number-average molecular weight
MV	molecular vector
MWD	molecular weight distribution
M <sub>w</sub>	weight average molecular weight
M <sub>z</sub>	Z average molecular weight
n <sub>i</sub>	number of mole of specie i
NCO	isocyanate chemical group on site 1
NCO'	isocyanate chemical group on site 2
OH	hydroxyl chemical group
p <sub>i</sub>	probability of event i
PPG	polypropylene glycol
r	NCO/OH ratio

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R	gas constant
R	random number
RSV	reaction space vector
SWV	species weight vector
TDI	toluene diisocyanate
t	time
T	temperature
V	volume
W(M)	mass fraction of molecular weight M
X	conversion
[ ]	concentration

$\eta', \eta''$	dynamic viscosity
$\eta^*$	complex viscosity
$\eta_0$	zero shear rate viscosity
$\lambda_e$	characteristic time
$\rho$	density
$\tau_i$	relaxation time
$\omega$	oscillatory frequency

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## 1.0 INTRODUCTION

The increasing use of composite materials in industries today continuously raises new challenges for the processing of thermoset polymers. In the field of military technology, composite products are found, besides the well-known aerospace applications, in many energetic materials. These include polyurethane-bonded composite explosives and solid rocket propellants. The development of new propellant formulations requires a thorough evaluation of all aspects of the material characteristics. One of them concerns the ability of the propellant to be casted into a defect-free propellant grain. In order to achieve this requirement, special care must be taken to optimize the processing cycle. When casting, the paste must retain enough fluidity to prevent void formation, while showing a sufficient consistency to avoid sedimentation.

Among the material functions of interest in the evaluation of solid rocket propellants, the viscosity-shear rate spectrum is of utmost importance (Ref. 1). Numerous techniques have been studied to correlate the observed rheology of the curing polymers with the progress of the polymerization reaction. Often, this chemorheological characterization is performed by adiabatic viscometry (Ref. 2). In such a case, the change in rheology is monitored and correlated with time. Unfortunately, these relations cannot be easily adapted for changes of the polymerization process parameters, such as temperature or catalyst concentration. In some instances, the viscosity has been reported as a function of the extent of reaction (Refs.3,4). This approach makes possible, with appropriate kinetics expressions, the prediction of how changes in the reaction conditions will effect the conversion and, therefore, the rheology of the polyurethane system.

However, the kinetic (or the deterministic) approach alone is unable to self-adjust to changes in the prepolymer to be cured. So different polyols will, for the same level of conversion, obviously have different rheologies, simply because their molecular weights will be different. This leads to the uneasy task of estimating the molecular weight of the polymer as a function of the extent of reaction. In fact, the whole molecular weight distribution must be found if one wants to obtain truly complete rheological information.

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In this memorandum, an application of stochastic simulation algorithms to the reaction of polyurethane systems found in rocket propellants is presented. The objective of the work described here is to demonstrate the usefulness of this methodology as a means of modeling the processing of reactive polymeric material. In this present study, the scope of the modeling is restricted to conversion up to the gel point. A numeric code in Fortran77 has been developed that allows calculations on multi-component polyol-polyisocyanate mixtures. The core of the software will run on any platform being able to compile ANSI FORTRAN77 code, while the graphics interface modules included are specific to Apple Macintosh® operating systems. Experiments have been carried out to validate the numeric simulations. Three different were systems considered: HTPB-TDI, PPG-HDI and GAP-IPDI.

This technical memorandum reports work done at DREV between January 1994 and December 1994 under project PSC 32C, Missile Propulsion.

## 2.0 THEORY

### 2.1 Description of the time behavior of a chemical reaction

The problem of describing the evolution of a chemically-reacting system is mathematically addressed by establishing appropriate time functions for concentrations of each species found in the reaction space. As Gillespie (Ref. 5) pointed out, this is generally accomplished through either a deterministic or a stochastic approach.

The deterministic point of view is the more usual way of describing the kinetics of a chemical reaction. Generally, the rate of change for the population of each of the  $n$  components of a system is expressed by an equation like:

$$\frac{dX_i}{dt} = f(X_1, \dots, X_n) \quad [1]$$

Hence, the overall behavior of the reaction is given by a set of  $n$  ordinary differential equations. Often, an analytical solution of the problem is impossible to achieve and extensive numerical methods have to be used (Ref. 6) to solve equation [1].

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The effectiveness of the reaction rate equations to evaluate the kinetics has been demonstrated for an impressive number of reactive systems. However, it must be kept in mind that, mathematically, this method interpolates a continuous function over a physically-discrete phenomenon. Indeed, the molecular populations of a reaction space cannot evolve by a quantity other than the number (integer) of molecules taking part in a reaction. Fortunately though, for most problems, this quantum limitation can be overlooked.

The stochastic approach considers the evolution of a chemical reaction as the macroscopic result of a purely random series of events taking place at the molecular scale. Fundamentally, the description of the time-dependent process is given by a distribution of probability functions for each elementary reaction occurring within the reaction space. These functions will have to be defined by simple formulations based on the levels of species forming the reaction space population. Whenever possible, a prior knowledge of the reaction pathway will be helpful. The probability distributions are thereafter used either in a master probability equation or in Monte-Carlo simulations. This shall be discussed in section 2.4. Examples of the use of the stochastic determination of reaction kinetics have been reported to solve problems related to inorganic, pharmaceutical and polymer materials chemistry (Refs. 5-10).

## 2.2 Effect of molecular weight on rheological properties

There is an intimate relation between the size of polymer chains in the liquid state (or concentrated solution) undergoing shear flow and their material functions. The most-often studied of these rheological properties, viscosity, is affected by the rate of shear applied on the material. Typically, for the range of shear rate found in polymer mixing processes, the viscosity - shear rate spectrum plotted on a logarithmic scale will have a plateau portion at lower shear rates followed by a linear negative slope. These two sections of the spectrum are often referred to as the zero shear rate viscosity (Newtonian) and the power-law index (shear thinning). Both are affected by the size of the polymer molecule. The zero shear rate viscosity ( $\eta_0$ ) changes as a power of the molecular weight ( $M$ ). For monodisperse polymers, the following relation holds (Ref. 11):

$$\eta_0 \propto M^a \quad [2]$$

where  $1 < a < 2.5$  for  $M < M_e$   
 $a = 3.4$  for  $M > M_e$

It is seen that beyond the molecular weight of entanglement ( $M_e$ ) the relation between  $\eta_0$  and  $M$  will always be the same, regardless of the considered species. Accordingly, a fully logarithmic plot of the zero shear rate viscosity against the molecular weight will exhibit two straight lines with different slopes crossing at  $M_e$ . For polydisperse polymers, the weight-average molecular weight ( $M_w$ ) of the species shall be used in equation [2] (Ref. 12). These relations have proved to be remarkably suitable for a very large number of linear or slightly branched polymers.

Even though the zero shear rate viscosity is the primary material function used for characterization and simulation purposes, the dependence of  $\eta_0$  on shear rate must also be known if one wants to describe a chemical process where a wide spectrum of shear rates are applied to the polymer, as with rocket propellant mixing. In such a case, it may be useful to describe the transition between the Newtonian regime to the shear thinning behavior by a characteristic time ( $\lambda_e$ ) based on molecular weight ( Refs. 12-14):

$$\lambda_e = \frac{\eta_0 M}{\rho RT} \quad [3]$$

Again, unfortunately, some limitations arise from the fact that the slope of the power-law region may change with  $\lambda_e$ , in such a way that a theoretical-based correlation is difficult to establish.

Recently, Tsenoglou (Ref. 15) and Mead (Refs. 16, 17) have studied the relationship between molecular weight and relaxation time spectrum of polydisperse homopolymers. Mead has shown that equivalent information was stored in the molecular weight distribution (MWD) of a polymer and in its time relaxation spectrum, given that numerical interconversion was possible. This can be accomplished by the following procedure:



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- 1- simulate (or assume, or measure) a MWD
- 2- evaluate the relaxation time spectrum (  $G_{blend}(t)$  ) by:

$$\sqrt{\frac{G_{blend}(t)}{G_N}} = \int_{M_e}^{\infty} W(M) \sqrt{F(M,t)} dM \quad [4]$$

where  $\sqrt{F(M,t)}$  is the monodisperse species relaxation time function. Often, when no experimental data are available, this is expressed by an exponential of the form:

$$\sqrt{F(M,t)} = e^{\{-2tKM^{3.4}\}} \quad [5]$$

- 3- from the relaxation spectrum, the dynamic material functions are easily found by:

$$G'(\omega) = \omega \int_0^{\infty} G_{blend}(t) \sin(\omega t) dt \quad [6]$$

$$G''(\omega) = \omega \int_0^{\infty} G_{blend}(t) \cos(\omega t) dt \quad [7]$$

$$G'(\omega) = \eta'' \omega \quad [8]$$

$$G''(\omega) = \eta' \omega \quad [9]$$

- 4- finally the steady shear viscosity is estimated by the Cox-Mayer rule (Ref. 12) and the definition of the zero shear rate viscosity:

$$\eta \equiv \eta^* = \eta'(\omega) \left[ 1 + \left( \frac{\eta''}{\eta'} \right)^2 \right]^{0.5} \quad [10]$$

$$\eta_0 = \int_0^{\infty} G(t) dt = \sum_i^N G_i \tau_i \quad [11]$$

Of course, the completion of this procedure requires numerical methods for the solving of Fredholm integral equations of the first kind that will not be presented into this memorandum. However, it shall be seen that the primary motivation for evaluating the MWD through Monte-Carlo simulation lays in the potential rheological information generated by this process.

### 2.3 Statistical estimation of lower moments of the molecular weight distribution

It has been established that a function like a molecular weight distribution can be rigorously described by all of its integration moments (Ref. 17). However, for polymer science and polymer processing, only the fourth first moments are usually retained for characterization purposes. These are:

i) zero moment:

$$M_0 = \sum_i^N n_i M_i \quad [12]$$

it simply states that the molecular weight distribution must be closed for the species' mass fractions.

ii) first moment:

$$M_n = \frac{\sum_i^N n_i M_i}{\sum_i^N n_i} \quad [13]$$

often referred to as the number-average molecular weight

iii) second moment:

$$M_w = \frac{\sum_i^N n_i M_i^2}{\sum_i^N n_i M_i} \quad [14]$$

usually known as the weight-average molecular weight

iv) third moment:

$$M_z = \frac{\sum_i^N n_i M_i^3}{\sum_i^N n_i M_i^2} \quad [15]$$

simply called the Z- average molecular weight ( $M_z$ )

The determination of these moments of the MWD as a function of the advancement of a polymerization reaction has been studied via different methods over the last 40 years. Some of them, found in open literature, will be presented below.

The zero moment is clearly trivial to verify. The first moment can always be calculated by simple stoichiometry. For example, one may consider a polymerization reaction where:



where  $A_2$  and  $B_2$  are a diol prepolymer and a difunctional isocyanate respectively. This results in the formation of a polyurethane. The number-average molecular weight at a particular instant of the reaction is the total mass over the total number of molecules. For the previous reaction this translates by:

$$M_n = \frac{M_{A_2} + M_{B_2} r}{1 + r - 2X} \quad [16]$$

where:

$$r = \frac{n_{B_2}^0}{n_{A_2}^0} \quad [17]$$

and

$$X = \frac{n_{A_2}^0 - n_{A_2}}{n_{A_2}^0} \quad [18]$$

The second moment of MWD requires a more challenging analysis for its determination. Early researchers such as Stockmayer (Ref. 18) used extensive algebraic manipulations

based on probability distributions to deduce a typical expression for polycondensation. Keeping the same example for simplification, the appropriate expression is:

$$M_w = \frac{(1/r) \left(1 + \frac{X^2}{r}\right) M_{A_2}^2 + \left(1 + \frac{X^2}{r}\right) M_{B_2}^2 + \frac{4XM_{A_2}M_{B_2}}{r}}{\left(\frac{M_{A_2}^0}{r} + M_{B_2}^0\right) \left(1 - \frac{X^2}{r}\right)} \quad [19]$$

In the case of a polydisperse prepolymer, Ziegel et al (Ref. 19) found that this relation can be expressed by:

$$M_w = \frac{(1/r) \left(1 - \frac{X^2}{r}\right) M_{n_{A_2}} M_{w_{A_2}} + \left(1 - \frac{X^2}{r}\right) M_{B_2}^2 + \frac{2X}{r} \left(XM_{n_{A_2}}^2 + \frac{X}{r} M_{B_2}^2 + 2M_{n_{A_2}} M_{B_2}\right)}{\left(\frac{M_{n_{A_2}}}{r} + M_{B_2}\right) \left(1 - \frac{X^2}{r}\right)} \quad [20]$$

Later Macosko et al (Refs. 20, and 21) carried out a generalization of this procedure with a much simpler analysis based on the expectancy of probabilities for a defined configuration.

The moments predicted by these mathematical techniques have been confirmed for many polymeric systems by experimental analytical tools like GPC, tonometry, viscometry, etc. They are particularly useful for estimation of gel points in polymerization reactions. Unfortunately, they are not as reliable for high degree of conversion. In such situations, the mechanisms of molecular species diffusion must be considered. Gupta et al (Ref. 10) have demonstrated the use of Monte-Carlo simulations in polymerization reactions where diffusion must be accounted for. In these simulations, the spatial arrangement of each species was stored in memory in order to assess the probability of a reaction between two reactive sites based on the distance between them. Unfortunately this requires a fairly large amount of computational effort. The approach presented in this

memorandum is similar with regards of the Monte-Carlo algorithm but the computation task is greatly reduced by the equireactivity assumption since no records of the molecule positions are kept. However, time progress of the reaction is monitored.

#### 2.4 Stochastic algorithm describing polymerization reaction

The simulation approach presented here makes use of a Monte-Carlo technique. In order to achieve a description of a whole polymerization process, elementary steps, or events defining it have to be known. After that, the relative probability of each event has to be evaluated. Successive repetition of randomly chosen events suffice to describe the polymerization process.

Consider the reaction described in section 2.3, where one of the two functional groups of the isocyanate has a different reactivity. In such a case, three events can take place:

- a reaction between an OH group and a NCO group (event 1)
- a reaction between an OH group and a NCO' group (event 2)
- no reaction at all; only time elapses (event 3).

Accordingly, each event will have to be selected upon its probability, or frequency, of occurrence. If a random number is distributed between 0 and 1, then three intervals can be defined as:

$$[0, p_1] , [p_1, p_1 + p_2] \text{ and } [p_1 + p_2, 1]$$

where

$$p_1 = \frac{P_{event1}}{P_{event1} + P_{event2} + P_{event3}} \quad [21]$$

and similarly for  $p_2$  and  $p_3$ . It results that if  $R$ , a random number describing the  $i^{th}$  event, is part of the interval  $[0, p_1]$ , then event 1 will occur, and so on. The difficult task

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is to estimate  $p_{event\ i}$ . Often, when physical considerations are not explicit enough, one has to go back to traditional kinetics information. Hence, the apparent rate constants can make very acceptable approximations of event probabilities. For the situation described before, the apparent reaction rate equations are expressed by (Ref. 22) :

$$\frac{\Delta[\text{NCO}]_1}{\Delta t} = k_1[\text{OH}][\text{NCO}]_1 \quad [22]$$

$$\frac{\Delta[\text{NCO}]_2}{\Delta t} = k_2[\text{OH}][\text{NCO}]_2 \quad [23]$$

Considering that a single reaction event involves  $1/F$  mole of each species within a reaction space of volume  $V$ , then

$$\Delta[\text{NCO}]_1 = \Delta[\text{NCO}]_2 = \frac{1}{FV} \quad [24]$$

and the incremental time for each event is given by:

$$\Delta t_1 = \frac{1}{k_1 FV[\text{OH}][\text{NCO}]_1} \quad [25]$$

$$\Delta t_2 = \frac{1}{k_2 FV[\text{OH}][\text{NCO}]_2} \quad [26]$$

$$\Delta t_3 = \text{arbitrary constant} \quad [27]$$

It is obvious that the most probable event should have the smaller time increment, so the normalized probability of events for this reaction scheme will be expressed by:

$$p_i = \frac{1/\Delta t_i}{1/\Delta t_1 + 1/\Delta t_2 + 1/\Delta t_3} \quad [28]$$

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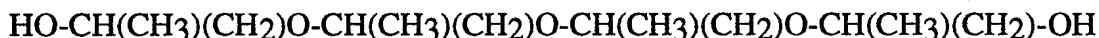
### 3.0 CODE DEVELOPMENT

#### 3.1 Molecular digitization

The simulation of a polymer chemical reaction by stochastic modeling asks for a translation, or an encoding, of the molecular structure information to a numerical data bank to be manipulated by the code. For this work, an approach adapted from Pandit *et al.* employing a well-known methodology (Ref. 7) has been retained. It consists of expressing the material domain by three vectors: the reaction space vector (RSV), the species weight vector (SWV), and the link weight vector (LWV). These quantities are described below.

##### 3.1.1 The reaction space vector

The reaction space vector contains the numerical translation of all the information about the molecular structure of every species found in the reacting system. This is done by assigning a number to each kind of elementary group forming a molecular species. An elementary group is considered to have no internal links affected by a chemical reaction. For example, an oligomer of polypropylene glycol (PPG) like :



would have a numeric equivalent of

$$\{0,4 \times 4,1\} = \{0,16,1\}$$

The conversion from molecular to vectorial representation is performed by using the key described in Table I. It is seen that each hydroxyl group is translated to the numeric value of 0 or 1, while successive monomer body groups expressed by 4's are summed to reduce the length of the RSV.

Inversely, a form like {0,12,3,5,2} would correspond, for a PPG-HDI system, to a molecule like



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Finally, the RSV will be constructed by sequentially adding each species vector. Henceforth, for a reaction space containing at some instant of the polymerization process these five chemical species:

{0,12,1}, {1,12,3,5,2}, {2,5,2}, {2,5,3,16,3,5,2} and {1,8,3,5,3,16,0}

the resulting RSV is:

{0,12,1, 1,12,3,5,2, 2,5,2, 2,5,3,16,3,5,2, 1,8,3,5,3,16,0}

It shall be noted that any particular species of the reaction space vector can be tracked back by using the fact that each of them must end by an OH or a NCO group.

TABLE I

Numerical Conversion Key for Typical Systems

Group Number	Molecular Group for HTPB-TDI system	Molecular Group for PPG-HDI system	Description
0	-	OH	prim. hydroxyl
1	OH	OH	hydroxyl
2	NCO para	NCO	isocyanate
3	NH-CO-O	NH-CO-O	urethane
4	CH <sub>2</sub> CHCHCH <sub>2</sub>	CH(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>0</sub>	monomer body
5	phenyl	(CH <sub>2</sub> ) <sub>6</sub>	isocyanate body
6	NCO ortho	-	isocyanate

### 3.1.2 The species weight vector

The species weight vector contains the amount (in moles) of each species found in the RSV, keeping the same relative position in the vectors. Therefore the third element of the SWV is the mass of the third species found in the RSV.



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A typical SWV for the RSV expressed before would be:

{ 1.1, 0.09, 1.0, 0.12, 0.3}

### 3.1.3 The link weight vector

The link weight vector completes the set of reactor space descriptors. It consists of the molar amount of each particular chemical link between elementary groups used to build the RSV. Accordingly, if five different kinds of links are found, five elements will constitute the LWV. Table II summarizes chemical links to be monitored (numerically) for two-component polyurethane systems. The LWV is calculated directly from the information encoded into the RSV and the SWV. For the previous example, and using the key of Table II, the resulting LWV is

{1.4, 1.49, 4.24, 2.3, 0.0, 0.93, 0.93}

**TABLE II**

Equivalence Table for Chemical Linkage

Position in the LWV	Groups Involved	Link type
1	0- 4	prim. hydroxyl - monomer body
2	1 - 4	sec. hydroxyl - monomer body
3	4 - 4	monomer - monomer body
4	2- 5	isocyanate - isocyanate body
5	5- 6	isocyanate body - isocyanate
6	3 - 4	urethane - monomer body
7	3 - 5	urethane - isocyanate body

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### 3.2 Performing a reaction

Within the frame of this particular study, only condensation reactions from an hydroxyl group with an isocyanate function, to form an urethane linkage, have been considered. Consequently, the total number of reactions of different kinds susceptible to take place into the reaction space is directly related to the number of different (non-chemically equivalent) OH and NCO functions among all the species. For a system with  $N_{OH}$  different hydroxyl functions and  $N_{NCO}$  different NCO functions the total number of chemical reactions is simply:

$$N_{CR} = N_{OH} N_{NCO} \quad [29]$$

Often, hydroxyl functions of a polydisperse polymer are considered to be equivalent, with no regards to the molecular weight of a particular species of the molecular weight distribution (MWD). In such a case, the number of possible chemical reactions will be imposed by the isocyanate population. For example, with the HTPB-TDI system, the TDI species bears two different NCO groups, since the reactivity of the ortho group is much less than that of the para- position NCO function. Hence, there are two possible reactions to consider. It has been discussed in section 2.4 how the choice of the reaction occurring at a step of the simulation path is performed.

Once the reaction type has been selected, the reaction sites have to be chosen. This is done on the basis that the probability of having a species reacting with another is directly proportional to the amount (mass) of this species found into the reaction space. So, if a OH - NCO reaction is to be performed, it is likely that the molecular species of the polydisperse polymer having the highest mass fraction has more chance to react. But this does not mean that it will actually be the selected site for the reaction (since the probability of having a particular species involved in a specific reaction is always less than one).

After the selection of the two reacting species, a copy of their molecular vector (MV) is extracted from the RSV:

Molecule bearing the hydroxyl reaction site:  $\{1,12,1\}$

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Molecule bearing the isocyanate reaction site: {2,5,2}

The chemical reaction between these sites is numerically simulated by forming a new molecular vector incorporating the new link formed:

New molecule: {2, 5, 3, 12, 1}

If the molecule formed is new to the reaction space, it will be added in the RSV at an index position based on its molecular weight. After that, the elements of the SWV and LWV are adjusted to the magnitude of the amount of material being reacted at each event. When less than 1/F mole of a particular species is left, it is removed from the RSV and the remaining amount of moles are transferred to its right hand side neighbor within the RSV.

### 3.3 Algorithm and software

A simplified algorithm of the numerical code developed for this project is shown in Figure 1. The complete program listing with variable definitions can be found in Appendix A. Except for some graphical interface functions included in Macintosh specific subroutines, the code is ANSI FORTRAN77 standard. The implementation of the stochastic logic and the manipulation of reaction vectors are carried out in a modular way by an extensive use of subroutines. The program can handle a reactor space including more than 3000 different species (molecular weight) as long as the size of the RSV remains under 60 000 integer elements. These limitations result from memory resource considerations and could be overcome on a more powerful machine. The initial data required for each simulation are gathered within a text file read by the code at the beginning of the execution. The template for this data file is included in Appendix B. The code has been used to simulate stochastic processes comprising up to five different events. However, more complex situations could also be studied with minor modifications. The results of the simulations are saved in two output files: poly.res and polyds.res. The first file includes the time evolution of  $M_n$ ,  $M_w$  and X while the second file reports the molecular weight distribution as a function of the conversion.

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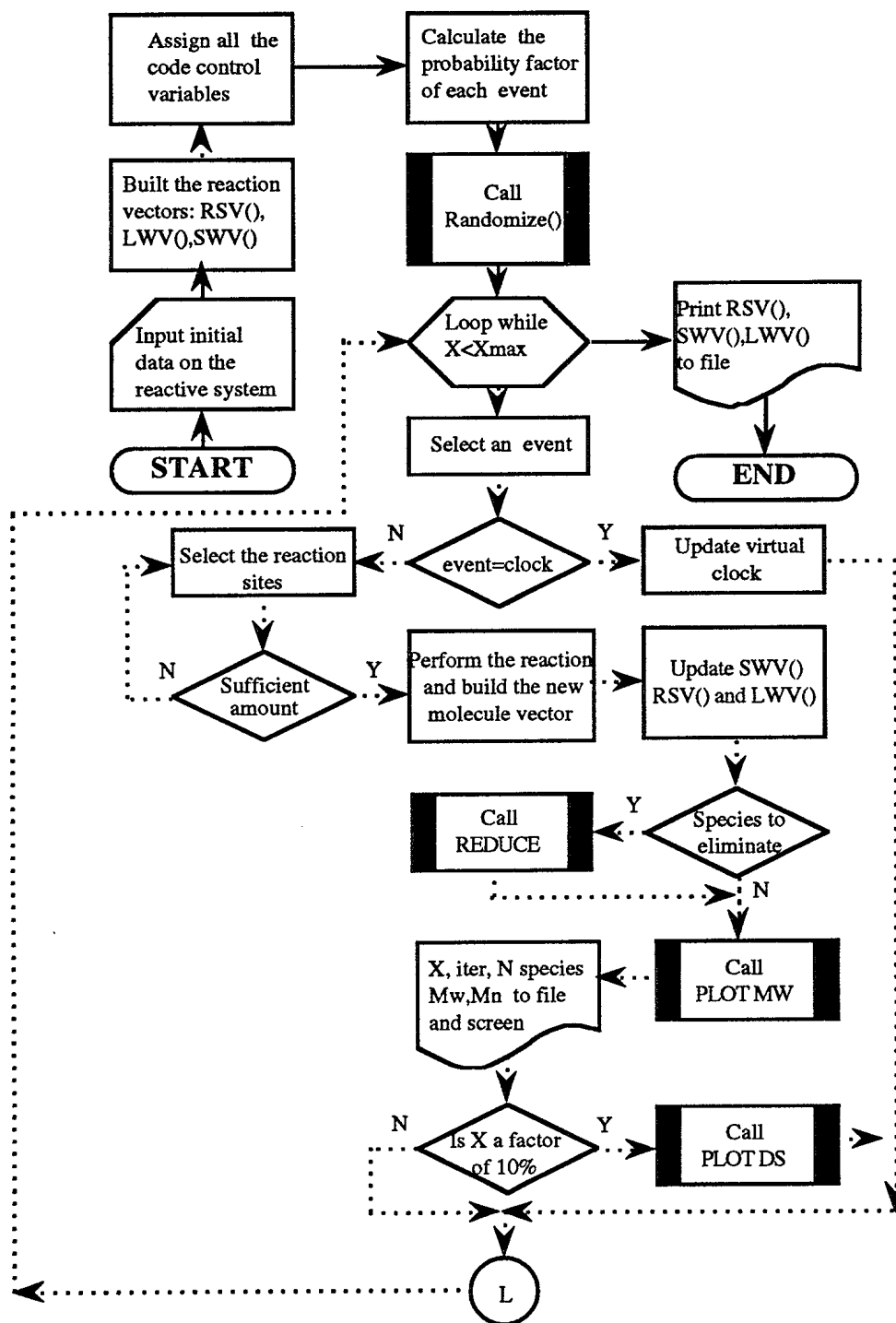


FIGURE 1 - Simplified Flowsheet of the Computer Code

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The program execution begins by evaluating an initial probability factor for each event before entering the main loop. Within this loop, successive random events will be chosen and performed until achievement of the desired level of conversion. Whenever the amount left of a particular species becomes smaller than the reaction event increment, the subroutine "REDUCE" is called to eliminate this species from each polymerization vectors. An on-screen progress of the simulation is given to the user by plots of  $M_n$ ,  $M_w$  and MWD. After completion, the user is prompted to print out the final screen layout. An example of printed screen is given in Appendix C.

One of the options given to the user by the code control variables is to obtain  $M_w - X$  and  $M_n - X$  plots for the considered system as calculated from Macosko formula (Refs. 20,21). For a system having reactive sites of the same reactivity, these curves should coincide with the same plots obtained by stochastic simulations.

## 4.0 SIMULATIONS

### 4.1 Comparative polyurethane systems

In order to evaluate the efficiency of the stochastic algorithm for the simulation of polyurethane polymerization, three different systems were considered: HTPB-TDI, PPG-HDI and GAP-IPDI. Their chemical structures are shown in Figure 2. In the HTPB-TDI reaction, the two isocyanate groups on the TDI do not exhibit the same reactivity. Hence, three stochastic events can take place: 1- reaction between an OH group and a NCO para-substituted (p-NCO); 2- reaction between an OH group and a NCO ortho-substituted (o-NCO) or 3- a clock event. For the PPG-HDI polyurethane, NCO at both ends of the hexane chain have the same reactivity, but the polypropylene glycol contains primary and secondary OH. Thus, the set of events in the reactor space is formed by: 1- reaction between a primary OH and a NCO group; 2- reaction between a secondary OH and a NCO group; or 3- a clock event. Finally, the GAP-IPDI system is very similar to the HTPB-TDI reaction, even though the difference in reactivity of the NCO groups is much less significant than with TDI. For each of the previous polyurethane systems, the probability of events was estimated from kinetics rate constants found in Table III. For

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some instances, these constants were not available for the conditions of the simulations and they had to be extrapolated from data reported in the references of Table III.

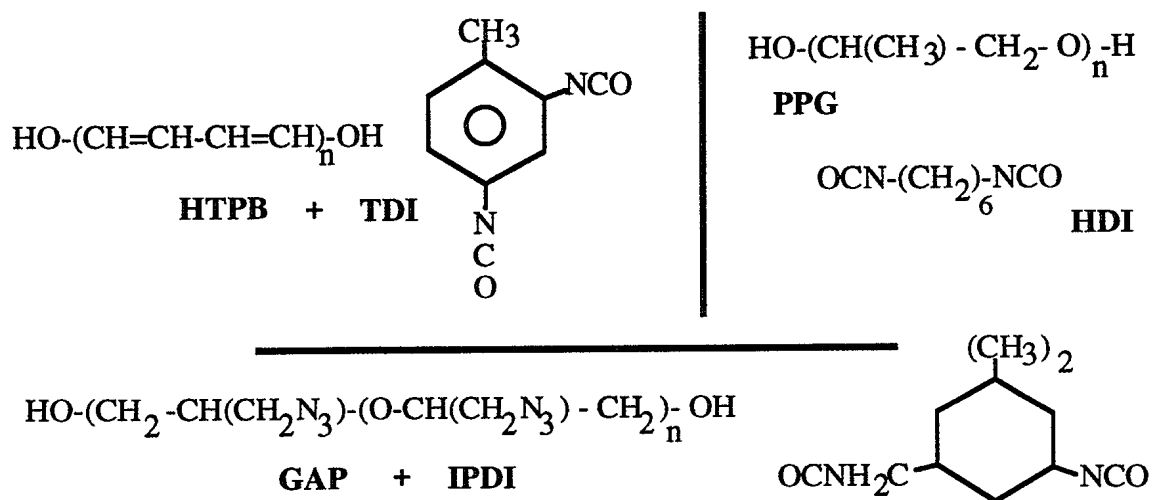


FIGURE 2 - Initial Components for each Polyurethane System

TABLE III

Rate Constants used for Probability Estimation

	reaction 1		reaction 2		ref.
	reaction type	k <sub>1</sub> (50 °C) (l/mol/min)	reaction type	k <sub>2</sub> (50 °C) (l/mol/min)	
HTPB-TDI	p-NCO, OH	.142	o-NCO, OH	.0035	22
PPG-HDI	prim. OH, NCO	.0015	sec. OH, NCO	.0005	23,24
GAP-IPDI	ring NCO, OH	.0004	meth. NCO, OH	.0003	23,24

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#### 4.2 Effect of polymerization reaction variables

The manipulated variables acting on the polyurethane formation reaction were, for the purpose of this study, the temperature and the NCO/OH ratio. It was expected that the temperature would affect not only the rate of reaction, but also the molecular weight distributions, for systems where a difference existed in the reactivity of reactive groups for the polyol or the polyfunctional isocyanate. On the other hand, the stoichiometry of the reaction determines the level of conversion where a rapid increase of the molecular weight is observed. For each of the systems described in section 4.1, a simulation was carried out for three levels of NCO/OH ratio: 0.8, 1.0 and 1.2. The effect of temperature was investigated only for the HTPB-TDI reaction.

The results of the simulations are represented by two curves: i) a plot of  $M_w/M_w^0$  against  $X$  with an overlay for the time - conversion response, and ii) the final molecular weight distribution at conversion level of 80%. These curves are shown in Figs. 3 to 8 for each of the three polyurethane systems.

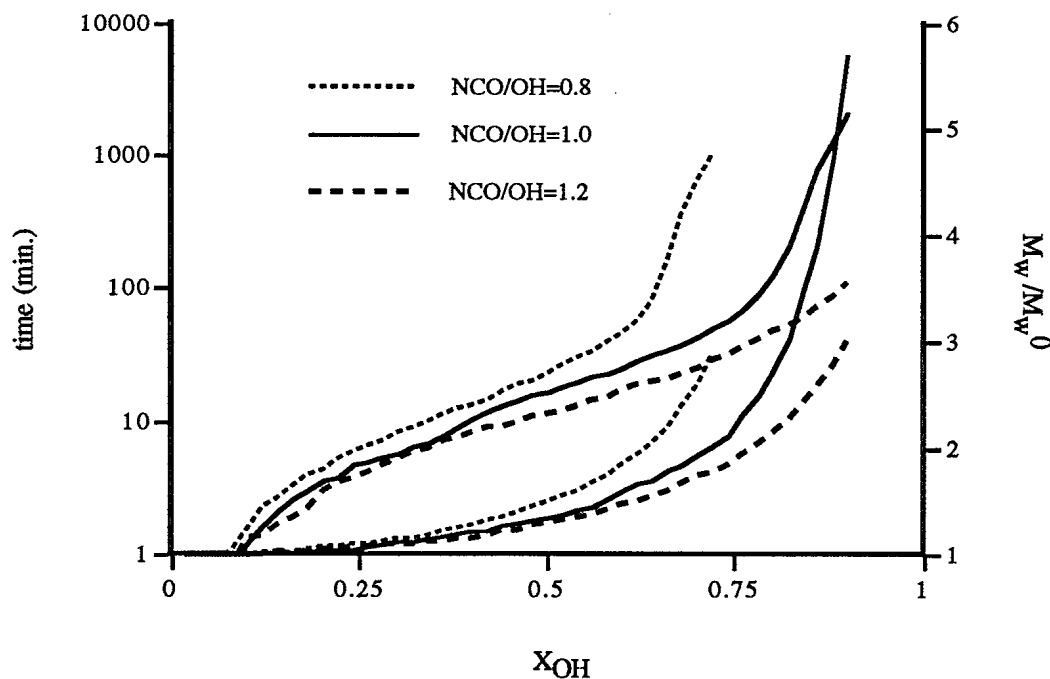


FIGURE 3 - Effect of NCO/OH ratio on HTPB-TDI polymerization at 50 °C

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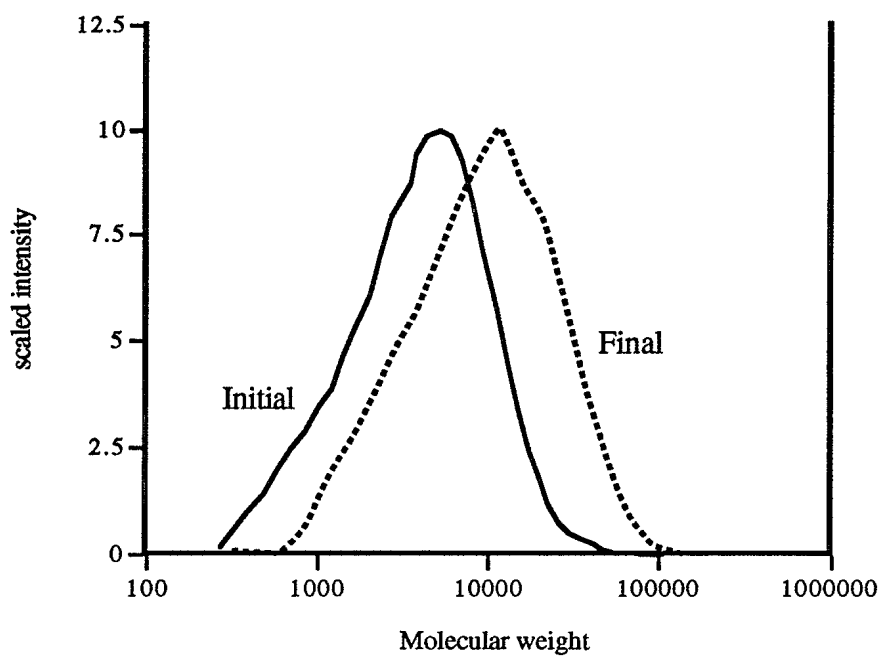
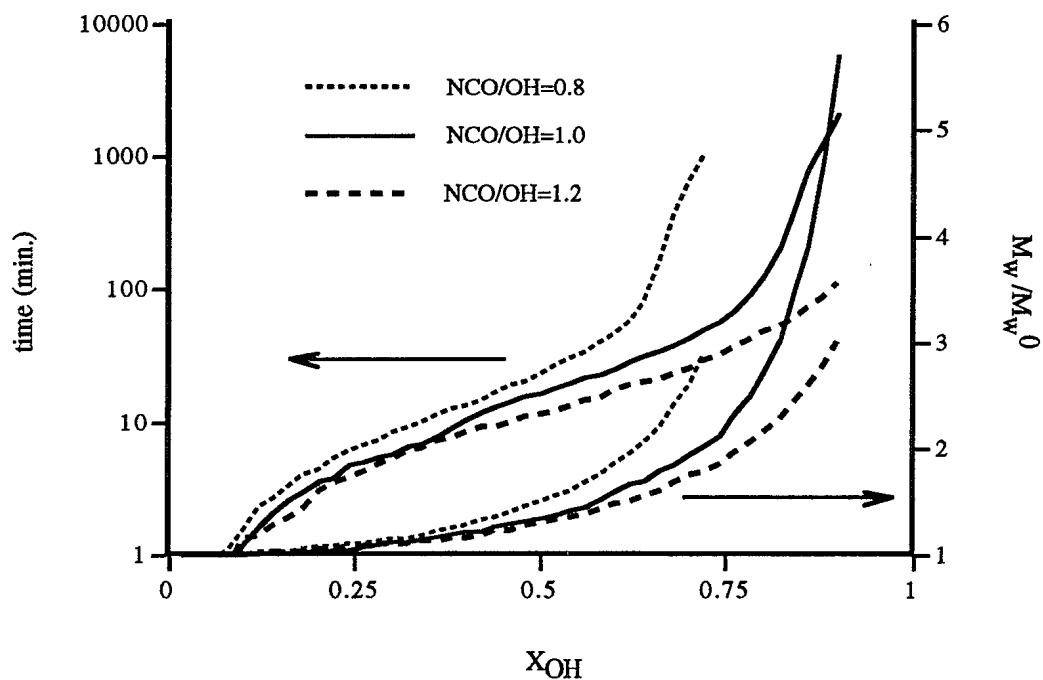
FIGURE 4 - MWD for HTPB-TDI polymerization ( $X=0.8$ ) at 50 °C, NCO/OH=1.0

FIGURE 5 - Effect of NCO/OH ratio on PPG-HDI polymerization at 50 °C



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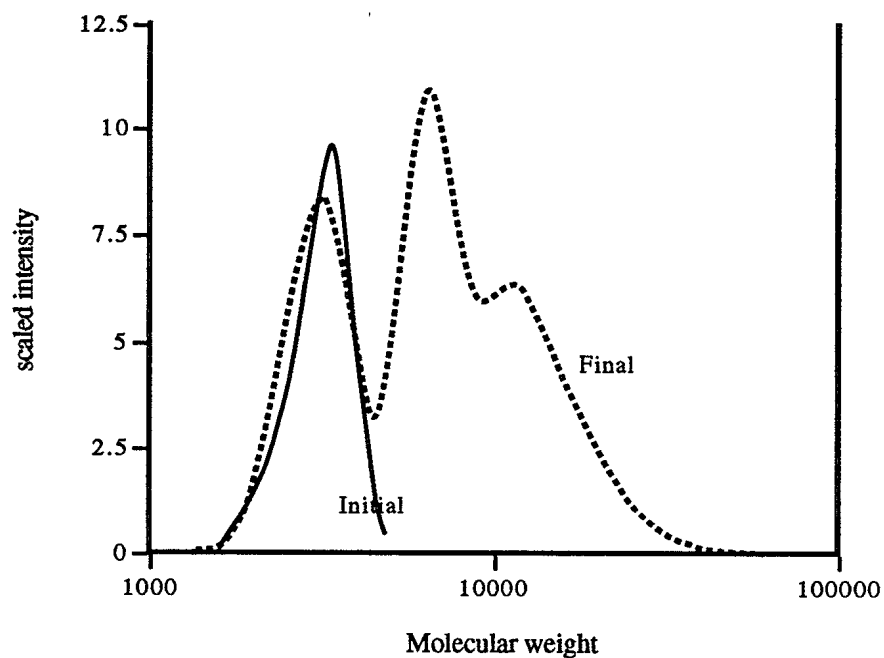


FIGURE 6 - MWD for PPG-HDI polymerization ( $X=0.8$ ) at 50 °C, NCO/OH=1.0

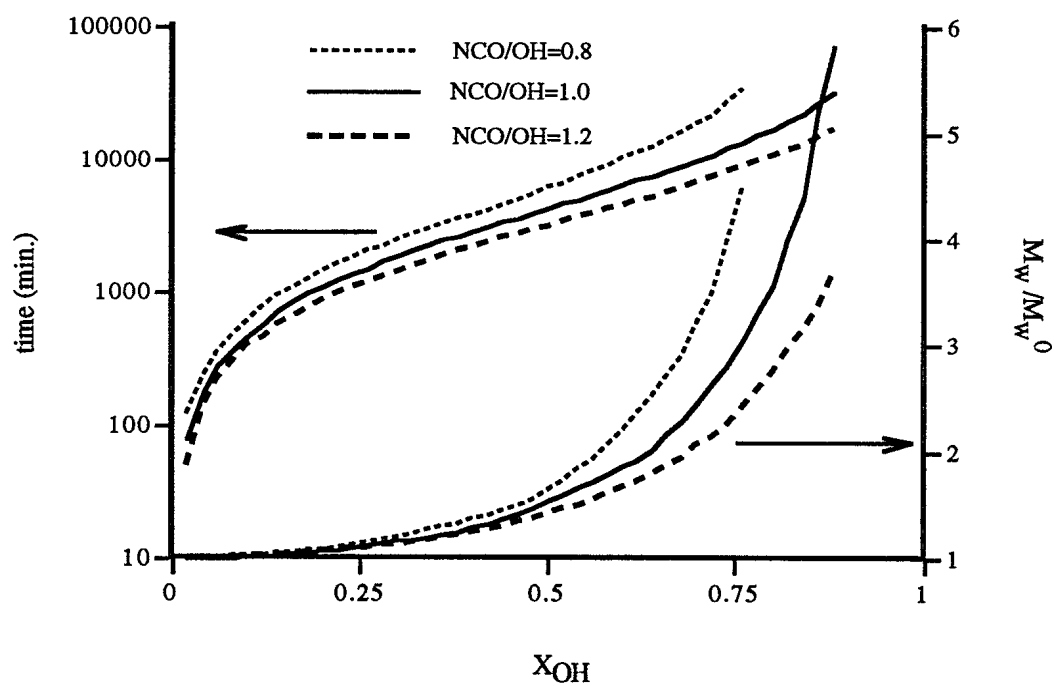


FIGURE 7 - Effect of NCO/OH ratio on GAP-IPDI polymerization at 50 °C

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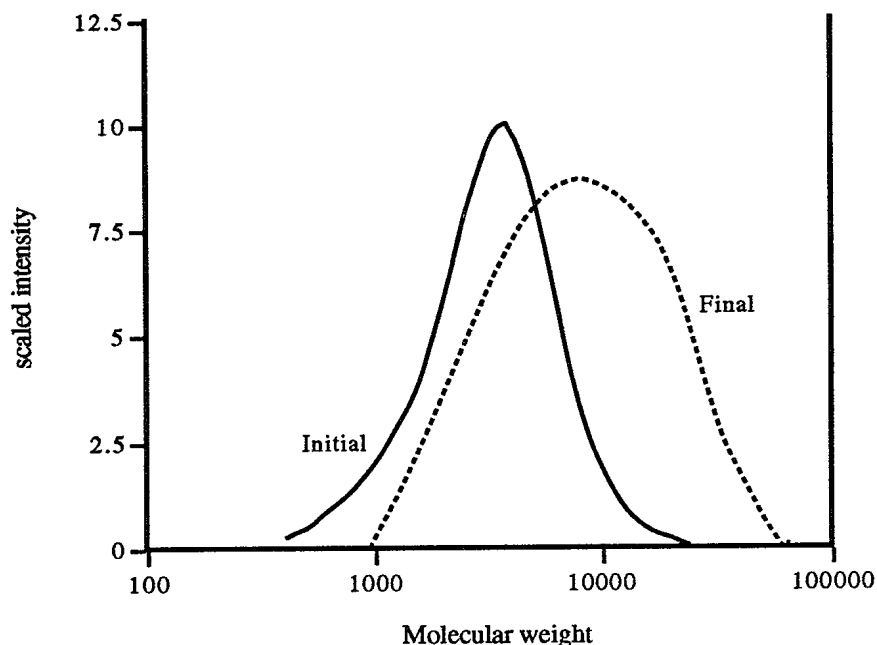


FIGURE 8 - MWD for GAP-IPDI polymerization ( $X=0.8$ ) at 50 °C, NCO/OH=1.0

## 5.0 EXPERIMENTAL

In order to carry out the stochastic simulations of the polyurethane binder formation, the initial molecular weight distribution of HTPB, PPG and GAP prepolymers had to be determined experimentally by gel permeation chromatography (GPC) based on a polystyrene calibration. The polyols, PPG (Aldrich Co.), HTPB R-45M (Arco Chemical) and GAP (3M) were used as received from the supplier. The water content of these materials was measured by Karl-Fisher titration and it was found to be below 0.05% for each polymer. The characterization of the prepolymer is reported in Table IV. For the PPG, a correlation was available to estimate the real molecular weight from the results obtained by polystyrene calibration (Ref. 25).

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TABLE IV

Characterization of Liquid Prepolymers

	Measured by GPC (polystyrene)			Supplier		
	M <sub>n</sub>	M <sub>w</sub>	polydispersity	M <sub>n</sub>	M <sub>w</sub>	polydispersity
HTPB	6220	12000	1.93	2600	7000	2.7
PPG <sup>1</sup>	3100	3200	1.03	3000	3250	1.1
GAP	2416	3810	1.57	2000	3200	1.6

1: Corrected by correlation:  $M_{ppG}=5.731 M_{ps}^{0.714}$

Moreover a limited number of experimental molecular weight determinations were performed on HTPB-TDI and PPG-HDI systems to assess the effectiveness of the computer code to simulate these processes. Since both systems were known to behave as an A<sub>2</sub>+ B<sub>2</sub> reaction, most of the polymerization products were soluble in an organic solvent at high conversion levels. The isocyanates were obtained from Aldrich Co. The polymerization was carried out in small beakers on a 50-g scale within a temperature-controlled oven. During the reaction, five or six 3-g samples were removed at unequally-spaced intervals of time. Each sample was quenched with an excess of diethylamine (DEA) to neutralize the remaining isocyanate. After adding the DEA, the level of conversion in the sample was measured by <sup>13</sup>C-NMR spectroscopy (Ref. 22) and the MWD was estimated by GPC in 4 successive WATERS Ultrastyrigel® columns of grade 10<sup>5</sup> (stock # 10574), 10<sup>4</sup> A (stock # 10573), 500 A (stock # 10571), and 100 A (stock # 10570).

## 6.0 DISCUSSION

At this point, it should be recalled that the interest of performing Monte-Carlo simulations on simple polymerization reactions was to obtain the MWD of these systems at any level of conversion before the gel point. A first step toward the validation of this work regards the comparison of lower moments of the MWD predicted by the software

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with those calculated from the Macosko and Stockmayer approach (Refs. 18, 20 and 21). For a system where each reaction site is known to have about the same reactivity, as for GAP-IPDI, it was found that stochastic results are in good agreement with the curves predicted by the more conventional approach.

It should also be noted that unequal reactivity will only affect  $M_w$  since  $M_n$  depends only on the number of molecules reacted, not their length. An example of this effect is shown in Figure 9 for stoichiometric HTPB-TDI polymerization at 30 °C. In this case, the NCO site in para position is expected to be 50 times more reactive than the ortho substituted NCO (Ref. 22). Thus, there is a chain elongation effect taking place that delays the weight average molecular growth. In accordance with this hypothesis, the results of the simulation are perfectly coherent.

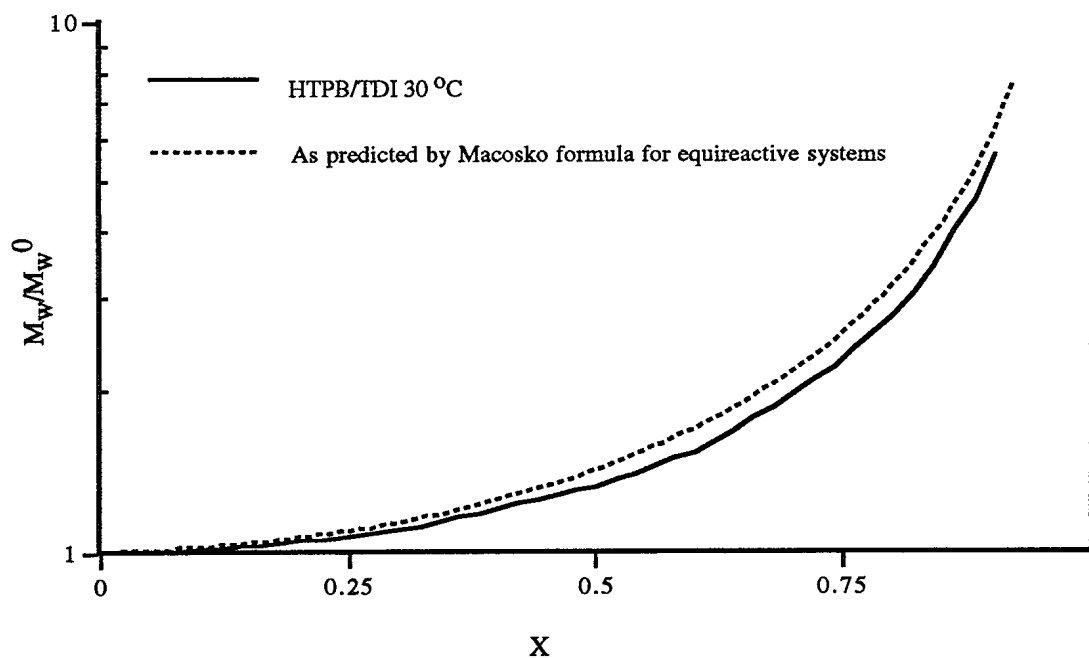


FIGURE 9 - Effect of asymmetrical reactivity on HTPB-TDI polymerization

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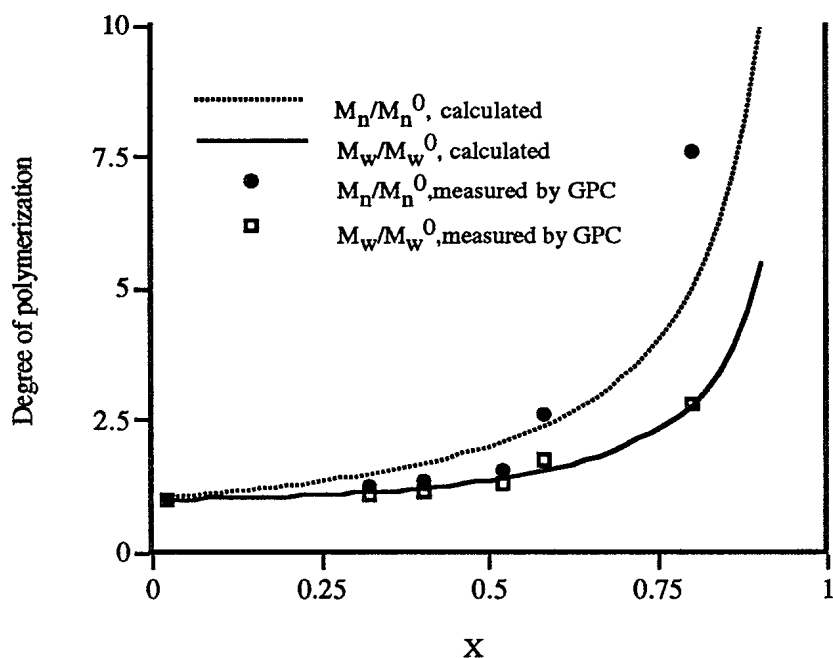


FIGURE 10 - Comparison between measured and calculated degree of polymerization for HTPB-TDI reaction at  $\text{NCO/OH} = 1.0$

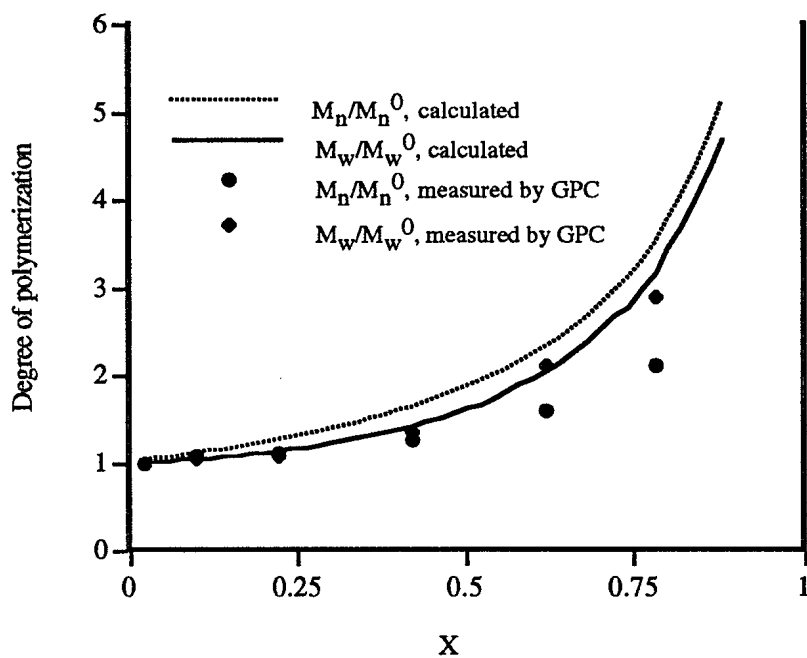


FIGURE 11 - Comparison between measured and calculated degree of polymerization for PPG-HDI reaction at  $\text{NCO/OH} = 1.2$

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As discussed in section 5, experiments have been carried out in the laboratory to compare the simulation results with real polymerization products. This comparison was based on  $M_n$  and  $M_w$  for HTPB-TDI and PPG-HDI systems. Figures 10 and 11 show that there exists a fairly good agreement for both systems between calculated and measured molecular weights except for high levels of conversion. The differences observed may be associated with the fact that the measurements were obtained from a polystyrene-calibrated GPC, since the factor between actual and measured molecular weight may change for higher molecular weight. This is also suggested by the fact that this difference is more important for the PPG-HDI curve, where the non-linear correlation available was developed for low-molecular-weight polymers.

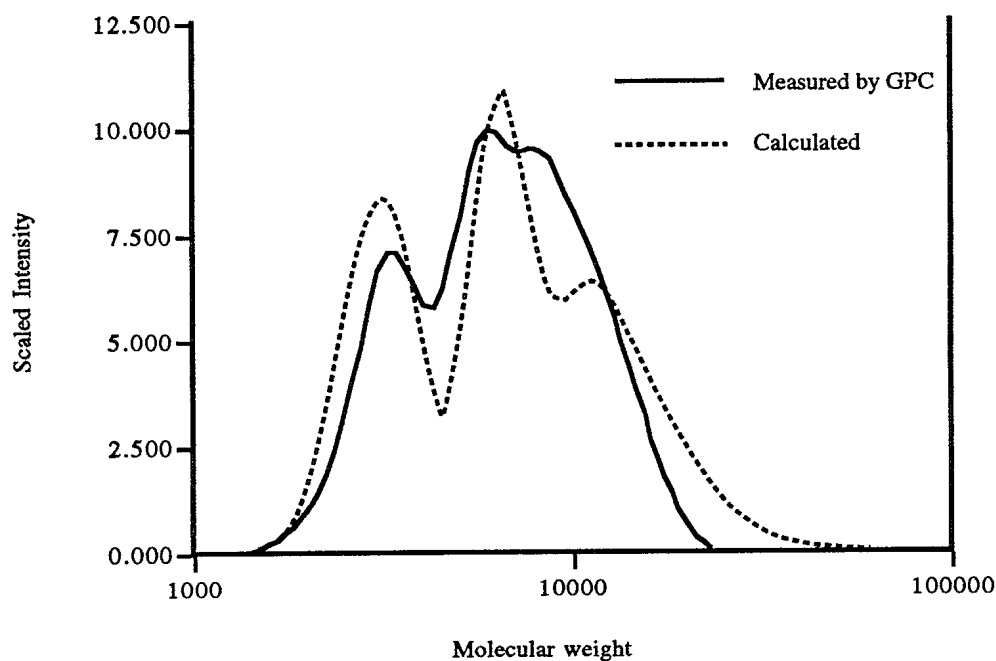


FIGURE 12 - Comparison between measured and calculated MWD for PPG-HDI system at NCO/OH=0.8

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Based on the fact that the calculated  $M_n$  and  $M_w$  appeared to satisfy experimental evidences, it is justified to assume that the whole MWD is reasonably well simulated by the software. However, one of the problems with the manipulation of the calculated MWD is to reconstruct a continuous distribution from a series of discrete mass fraction and individual molecular weights. This can be accomplished by usual regularization code with equation [12] as a constraint. Even without an extensive mathematical treatment, a simple comparison between calculated and measured MWD, as shown in Figure 12, reveals an acceptable similitude.

Another important issue to ensure a meaningful simulation was the frequency factor determining the amount of moles reacting during a single event. Based on an initial quantity of 100 moles of material, it was found that  $F$  should at least be greater than 100. This implies that 10000 reaction events were needed to achieve complete conversion. Because a greater  $F$  value translates into more species within the RSV, the calculated MWD is therefore closer to the real physical system where an extremely large number of different polymer chains are found. If only the  $M_n$  and  $M_w$  values are of some interest, a smaller  $F$  will still give results expected from Stockmayer's equation with a smaller computational effort. A typical run time for a simulation was about 30 minutes on a 68040 based personal computer.

## 7.0 CONCLUSIONS

Stochastic modeling has been used to simulate the polymerization of a diol with a diisocyanate for polyurethane systems similar to those found in solid rockets motors. The computer code developed for this purpose has proved to be reliable for the prediction of the MWD as a function of the level of conversion (advance of the reaction). This information about the molecular structure of a reacting system can be used to estimate the rheological behavior of these materials. This would allow a more detailed optimization of propellant formulations as well as a better design capability for their related industrial processing.

However, to achieve truly useful results, the same kind of algorithm would have to be adapted for systems with significant cross linking, that is, systems with overall equivalent functionality greater than 2 for the polyfunctional isocyanate and polyol. This

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would require minor modifications in the software for the encoding mode of information about the molecular structure of species in the reaction space.

In summary, it has been demonstrated that Monte-Carlo simulations offer a powerful, yet simple, mean of investigating the development of advanced polyurethane-based energetic materials with a minimum of experimental information. Accordingly, there is a great interest in pursuing the development of a numerical code that will allow the simulation of more complex systems, more representative of in-service propellant formulations. The work described in this memorandum will be followed by the experimental rheology characterization of solid rockets propellants and the modeling of the behavior of these systems will be accomplished using the results presented here.

## 8.0 ACKNOWLEDGMENTS

The author wishes to thank Dr. E. Ahad of the Chemistry and Environment Group for his valuable help in product analysis. Also thanks to Prof Abdellatif Aït-Kadi, from the Chemical Engineering Dept. of Laval University, for many thoughtful discussions.



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## **APPENDIX A**

### **Listing of the Computer Code for MWD Estimations**



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Page 1

```

C *****
C Software POLYFORT for molecular weight distribution estimation
C of polyurethane systems from stochastique simulations
C
C written in F77 by Charles Dubois
C
C version 1.1 April 6, 1995
C *****

GLOBAL DEFINE
  INCLUDE "Types.inc"
  INCLUDE "QuickDraw.inc"
  INCLUDE "Events.inc"
  INCLUDE "Controls.inc"
  INCLUDE "Windows.inc"
  INCLUDE "TextEdit.inc"
  INCLUDE "Dialogs.inc"
  INCLUDE "OSUtils.inc"
  INCLUDE "SegLoad.inc"
  INCLUDE "Files.inc"
  INCLUDE "StandardFile.inc"
  INCLUDE "Script.inc"
  INCLUDE "Packages.inc"
  INCLUDE "Printing.inc"
END

C -----
C CHECK Go/No go variable controlling loop exit
C COUNT Number of element within a reactive specie
C DEBUT,FIN Index of location of reacting specie within RSV
C DT Amount of a clock event
C F Frequency factor: amount of 1 reaction=1/F
C FL number of elements in the Reactor Space Vector
C H2,H3 height in pixel of window 2 and 3
C heure Dummy variable used for time display
C INSERT Specie index for the insertion of a new molecule
C iter Loop count
C IBODY Molecular weight of the isocyanate body
C itermax total number of iteration to acheive asked conversion
C JUMEAU Flag variable for existence of a similar Mw molecule
C K** Reaction rate constant of reaction **
C LINK() link weight vector
C L2, L3 length in pixel of window 2 and 3
C MW Weight average molecular weight
C Mn Number average molecular weight
C NT total number species found in the RSV
C MONO masse molaire d'un monomère
C MPOLY mass of polymer (moles)
C MISO mass of isocyanate (moles)
C NCOOH molar ratio of NCO group to OH group
C NCOPNT NCO link number of the reaction performed
C NEWV() vector of the molecule formed by the last reaction
C NISO Number of initial isocyanate species (1 or 2)
C NO- number of different OH group (1 or 2)
C OH-PNT OH link number of the reaction performed
C P1,P2,P3.. Probability of occurrence for each reaction
C POPUL(i,j) matrix where i= index of RSV and j= MW
C PROP molar fraction for isocyanate 1
C RSV() Reactor Space Vector
C SPECIE Index for do loop vectors scanning
C SPCOH Index for OH reacting specie
C SPCNCO Index for NCO reacting specie
C SX**,SY** échelle de trace pour les fenêtres 2 et 3
C SMV() Species weight Vector
C TIME Virtual time of the polymerization
C XMAX specified end of simulation conversion
C -----

PROGRAM polymer
  logical IMPRIME,MAC
  integer*2 RSV(60000),NEWV(20000)
  integer*4 CHECK,COUNT,DEBUT,FIN,FL,heure,HPACE,H2,H3,IBODY
  integer*4 INSERT,iter,itermax,JUMEAU,LAST,LDEBUT,LFIN,L2,L3,MONO
  integer*4 NISO,NOM,NOH,NT,OLDX(3),OLDY(3),PACE,POPUL(2,3000)
  integer*4 POIDS,SPECIE,SPCOH,SPCNCO,SITE,SOH,UNIT,OH
  real*4 SMV(3000),SN,MW,MN,SX2,SY2,SX3,SY3,MISO,MPOLY,NCOOH-,PROP
  real*4 LINK(7),XMAX,F,SOHCOH,OH-PNT,NCOPNT,RND,K1,K2,K3,K4,CHOIX
  real*4 SOHCO,TIME,DT,P1,P2,P3,P4,P5,PTOT,PCLOCK
  RECORD /WindowRecord/ window1 ! storage for a first window
  RECORD /WindowRecord/ window2 ! storage for a second window
  RECORD /WindowRecord/ window3 ! storage for a third window
  integer*4 ptr0,ptr1,ptr2,ptr3 ! pointers to each windows
  character*9 temps$
  character*30 frase$
  character*72 title$
  character*256 ISTRG$,RSTRG$ ! integer/REAL to string$ function
  character*256 StrZ55 ! fortran to pascal string function
  EXTERNAL StrZ55,ISTRG$,RSTRG$,RND !defined at end of this file
  COMMON POPUL,RSV,NEWV,SMV

C Get a pointer to the current (TEXTEDIT) window

```

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Hardisk:FORTTRAN STUFF:polymer11.f.5

Page 2

```

ptr0 = FrontWindow()
CALL ECRAN(2,20,500,279,639,'',ptr1,window1)
CALL POLICE(21,9,0)
frase$='EVENEMENT ='
CALL MoveTo(Val2(5),Val2(20))
CALL DrawText(frase$,Val2(0),VAL2(25))
frase$='Mn ='
CALL MoveTo(Val2(5),Val2(35))
CALL DrawText(frase$,Val2(0),VAL2(25))
frase$='Mn ='
CALL MoveTo(Val2(5),Val2(50))
CALL DrawText(frase$,Val2(0),VAL2(25))
frase$='X ='
CALL MoveTo(Val2(5),Val2(65))
CALL DrawText(frase$,Val2(0),VAL2(20))
frase$='nombre total d especes:'
CALL MoveTo(Val2(5),Val2(80))
CALL DrawText(frase$,Val2(0),VAL2(25))
frase$='taille du vecteur RSV:'
CALL MoveTo(Val2(5),Val2(95))
CALL DrawText(frase$,Val2(0),VAL2(25))
CALL INITTIME(ptr1)
temps$='000:00:00'
CALL SHOWTIME(temps$,ptr1)

CALL ECRAN(2,280,1,479,319,'',ptr2,window2)
CALL INITPLOT(ptr2,1,280,319,479,0.,1.,1000.,5.1E4,1,
+ SX2,SY2,L2,H2)
frase$='Mn or Mw vs X'
CALL MoveTo(Val2(120),VAL2(10))
CALL POLICE(21,12,1)
CALL ForeColor(Val4(409))
CALL DrawText(frase$,Val2(0),VAL2(2))
CALL ForeColor(Val4(33))
CALL DrawText(frase$,Val2(2),VAL2(3))
CALL ForeColor(Val4(341))
CALL DrawText(frase$,Val2(5),VAL2(4))
CALL ForeColor(Val4(33))
CALL DrawText(frase$,Val2(9),VAL2(5))

CALL ECRAN(2,280,320,479,639,'',ptr3,window3)
CALL INITPLOT(ptr3,320,280,639,479,10.,3.E5,0.,10.,0,5X3,SY3,
+ L3,H3)
CALL POLICE(21,12,1)
frase$='Mw Distribution'
CALL MoveTo(Val2(120),VAL2(10))
CALL DrawText(frase$,Val2(0),VAL2(16))

CALL SelectWindow(VAL4(ptr0))
CALL SetPort(VAL4(ptr0))
CALL InitCursor()
WRITE(6,*) 'APPUYEZ SUR RETOUR POUR LIRE UN FICHIER DE DONNEES'
PAUSE

```



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```

C .....
C
C Main program starts here
C .....

      MPOLY=50.
      TIME=0.
      X=0.

C .....
C LECTURE DES DONNEES A PARTIR D'UN FICHIER TEXTE
C .....

      OPEN(10,FILE='',STATUS='OLD',FORM='UNFORMATTED')
      READ(10,*) title$
      READ(10,*) F
      READ(10,*) XMAX
      READ(10,*) NCOOH
      READ(10,*) NISO
      READ(10,*) NOH
      READ(10,*) PROP
      READ(10,*) DT
      READ(10,*) K1
      READ(10,*) K2
      READ(10,*) K3
      READ(10,*) K4
      READ(10,*) IMPRIME
      READ(10,*) MAC
      READ(10,*) NT
      READ(10,*) MONO
      READ(10,*) IBODY
      DO I=1,NT
        READ(10,*) POPUL(2,I),SMV(I)
      END DO
      CLOSE(10)

C .....
C OUVERTURE D'UN FICHIER DE RESULTATS
C .....

      UNIT=11
      OPEN(11,FILE='poly.res',STATUS='OLD',FORM='FORMATTED')
      WRITE(UNIT,*) title$
      WRITE(UNIT,*) "DISTRIBUTION INITIALE"
      WRITE(UNIT,*) ' # ,Mw # ,Qté'
      DO I=1,NT
        WRITE(UNIT,10) I,POPUL(2,I),SMV(I)
      END DO

      OPEN(12,FILE='polyds.res',STATUS='OLD',FORM='FORMATTED')
      WRITE(12,*) title$

      CALL MOLECULE(NT,MONO,IBODY,MM,MN,SN,.FALSE.,0)
      CALL PLOTDS(NT,SX3,SY3,L3,H3,ptr3)

C .....
C FORMATION DES VECTEURS
C .....
C FUNCTIONAL GROUPS TABLE
C
C 0 FUNCTIONAL GROUP PRIM. OH
C 1 FUNCTIONAL GROUP SEC. OH
C 2 FUNCTIONAL GROUP NCO
C 3 FUNCTIONAL GROUP URETHANE
C 4 MONOMER
C 5 ISOCYANATE BODY
C 6 FUNCTIONAL GROUP NCO'
C .....

C FORMING THE REACTOR SPACE VECTOR

C POLYMER CHAINS FIRST

      NISO=MPOLY*NCOOH
      FL=0
      DO I=1,NT
        FL=FL+1
        IF(MOH.EQ.1) THEN
          RSV(FL)=1
        ELSE
          RSV(FL)=0
        END IF
        FL=FL+1
        RSV(FL)=4*POPUL(2,I)/MONO
        FL=FL+1
        RSV(FL)=1
        POPUL(2,I)=POPUL(2,I)+34
      END DO

C ISOCYANATE(S) FOLLOW(S)

```

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```

C
  FL=FL+1
  RSV(FL)=2
  FL=FL+1
  RSV(FL)=5
  FL=FL+1
  RSV(FL)=2
  IF (NISO.EQ.2) THEN
    FL=FL+1
    RSV(FL)=2
    FL=FL+1
    RSV(FL)=5
    FL=FL+1
    RSV(FL)=6
  END IF

C .....
C   FORMATION OF THE SPECIES WEIGHT VECTOR
C   SUR UNE BASE DE MPOLY DE POLYMER (OH) MISO MOLES
C   D'ISOCYANATE (NCO)
C .....

C   HYDROXYL CHAINS FIRST

  DO I=1, NT
    SWV(I)=SWV(I)/SN*MPOLY
  END DO

C   ISOCYANATE(S) FOLLOW(S)

  NT=NT+1
  SWV(NT)=MISO*PROP
  POPUL(2,NT)=IBODY+84
  IF (NISO.EQ.2) THEN
    NT=NT+1
    SWV(NT)=MISO*(1.-PROP)
    POPUL(2,NT)=IBODY+84
  END IF

C .....
C   FORMATION OF THE LINK WEIGHT VECTOR
C   LINK TABLE
C   LINK(1) = (0-4)   PRIM. OH-MONOMER
C   LINK(2) = (1-4)   SEC. OH-MONOMER
C   LINK(3) = (4-4)   MONOMER-MONOMER
C   LINK(4) = (2-5)   NCO-ISOCYANATE BODY
C   LINK(5) = (5-6)   NCO'-ISOCYANATE BODY
C   LINK(6) = (3-4)   URETHANE-MONOMER
C   LINK(7) = (3-5)   URETHANE-ISOCYANATE BODY
C .....

  DO I=1,7
    LINK(I)=0.
  END DO
  SPECIE=1
  LAST=RSV(1)
  DO I=2,FL
    NOW=RSV(I)
    IF((LAST.EQ.0.AND.NOW.EQ.4).OR.(LAST.EQ.4.AND.NOW.EQ.0)) THEN
      LINK(1)=LINK(1)+SWV(SPECIE)
    END IF
    IF((LAST.EQ.0.AND.NOW.GT.6).OR.(LAST.GT.6.AND.NOW.EQ.0)) THEN
      LINK(1)=LINK(1)+SWV(SPECIE)
    END IF
    IF((LAST.EQ.1.AND.NOW.EQ.4).OR.(LAST.EQ.4.AND.NOW.EQ.1)) THEN
      LINK(2)=LINK(2)+SWV(SPECIE)
    END IF
    IF((LAST.EQ.1.AND.NOW.GT.6).OR.(LAST.GT.6.AND.NOW.EQ.1)) THEN
      LINK(2)=LINK(2)+SWV(SPECIE)
    END IF
    IF (NOW.GT.6) LINK(3)=LINK(3)+SWV(SPECIE)*(FLOAT(NOW)/4.-1.)
    IF ((LAST.EQ.2.AND.NOW.EQ.5).OR.(LAST.EQ.5.AND.NOW.EQ.2))
      + LINK(4)=LINK(4)+SWV(SPECIE)
    IF ((LAST.EQ.6.AND.NOW.EQ.5).OR.(LAST.EQ.5.AND.NOW.EQ.6))
      + LINK(5)=LINK(5)+SWV(SPECIE)
    IF ((LAST.EQ.3.AND.NOW.EQ.4).OR.(LAST.EQ.4.AND.NOW.EQ.3))
      + LINK(6)=LINK(6)+SWV(SPECIE)
    IF ((LAST.EQ.3.AND.NOW.GT.6).OR.(LAST.GT.6.AND.NOW.EQ.3))
      + LINK(6)=LINK(6)+SWV(SPECIE)
    IF ((LAST.EQ.3.AND.NOW.EQ.5).OR.(LAST.EQ.5.AND.NOW.EQ.3))
      + LINK(6)=LINK(6)+SWV(SPECIE)
    IF ((LAST.EQ.4.AND.NOW.EQ.1).OR.(LAST.EQ.5.AND.NOW.EQ.2)
      + .OR.(LAST.EQ.5.AND.NOW.EQ.6)) SPECIE=SPECIE+1
    IF ((LAST.GT.5).AND.(NOW.EQ.1)) SPECIE=SPECIE+1
    LAST=NOW
  END DO

  WRITE(UNIT,*) "REACTOR SPACE VECTOR:"
  WRITE(UNIT,11) (RSV(I),I=1,FL)
  WRITE(UNIT,*) "SPECIE WEIGHT VECTOR:"
  WRITE(UNIT,12) (SWV(I),I=1,NT)
  WRITE(UNIT,*) "LINK WEIGHT VECTOR"
  WRITE(UNIT,13) (LINK(I),I=1,7)

```

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IF (XMAX.GT.NCOOH*100.) XMAX=NCOOH*100.
itermax=INT(XMAX*F)

CALL MOLECULE(NT,MONO,IBODY,MN,MN,SN,.FALSE.,NISO)
IF (MAC) THEN
  CALL MACOSKO(IBODY,MN,NCOOH,LZ,HZ,SKZ,SYZ,ptr2,NT,NISO,XMAX)
END IF
CALL MOLECULE(NT,MONO,IBODY,MN,MN,SN,.TRUE.,NISO)
OLDX(1)=INT(.1*LZ*X*SKZ)+1
OLDX(2)=OLDX(1)
OLDY(1)=H2-INT(.1*H2+MN*SYZ)-1
OLDY(2)=H2-INT(.1*H2+MN*SYZ)-1
CALL PLOTMH(X,MN,SKZ,SYZ,OLDX(1),OLDY(1),LZ,HZ,ptr2,409,2)
CALL PLOTMH(X,MN,SKZ,SYZ,OLDX(2),OLDY(2),LZ,HZ,ptr2,341,2)
WRITE(UNIT,*) 'incrément = ',1/F,' moles'
WRITE(UNIT,*) 'NT FLAG ITER X Mn Mw time (min)'
WRITE(6,*) 'incrément = ',1/F,' moles'

```

```

CALL RANDOMIZE()
CALL POP(FL,NT,MONO,IBODY)
I=1
DO WHILE(I.LE.NT)
  IF(SMV(I).LT.1/F) THEN
    CALL REDUCE(FL,NT,I,SITE,LINK,1)
  ELSE
    I=I+1
  END IF
END DO
PCLOCK=1./DT
iter=1
DO WHILE(iter.LE.itermax)

```

C SELECT AN EVENT

```

SITE=0
DO WHILE (SITE.EQ.0)
  P1=K1*LINK(2)*LINK(4)*F/150.
  P2=K2*LINK(2)*LINK(5)*F/150.
  P3=K3*LINK(1)*LINK(4)*F/150.
  P4=K4*LINK(1)*LINK(5)*F/150.
  PTOT=P1+P2+P3+P4*PCLOCK
  P5=PCLOCK/PTOT
  P4=P4/PTOT
  P3=P3/PTOT
  P2=P2/PTOT
  P1=P1/PTOT
  CHOIX=RND()
  IF (CHOIX.GT.(P1+P2+P3+P4)) THEN
    TIME=TIME+DT
  ELSE IF (CHOIX.GT.P1+P2+P3) THEN
    SITE=6
    OH=0
  ELSE IF (CHOIX.GT.P1+P2) THEN
    SITE=2
    OH=0
  ELSE IF (CHOIX.GT.P1) THEN
    SITE=6
    OH=1
  ELSE
    SITE=2
    OH=1
  END IF
  IF ((LINK(4).LE.1/F).AND.(SITE.EQ.2)) SITE=0
  IF ((LINK(5).LE.1/F).AND.(SITE.EQ.6)) SITE=0
END DO

```

C

C

C LOCATION OF THE REACTION SITES

```

CHECK=0
DO WHILE (CHECK.EQ.0)
  SPCOH=0
  OHPNT=LINK(1+OH)*RND()
  SPCOH=0
  IF (SITE.EQ.2) THEN
    NCOPNT=LINK(4)*RND()
  ELSE
    NCOPNT=LINK(5)*RND()
  END IF
  SOMOH=0.
  SOMNCO=0.

```

C

```

RECHERCHE DE L ESPECE OH
IF (RSV(1).EQ.OH) SOMOH=SOMOH+SMV(1)
IF (SOMOH.GE.OHPNT) THEN
  fn=1
  SPCOH=1
  DEBUT=POPUL(1,1)
  HFACE=-1
END IF
IF (RSV(POPUL(1,1)) EQ.OH .AND. SPCOH.EQ.0)

```

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```

+      SOMOH=SOMOH+SMV(1)
      IF (SOMOH.GE.OHPNT) THEN
        fin=POPUL(1,1)
        SPCOH=1
        DEBUT=1
        HPACE=1
      END IF
      I=2
      DO WHILE ((SPCOH.EQ.0).AND.I.LE.NT)
        IF (RSV(POPUL(1,I-1)+1).EQ.OH)
+      SOMOH=SOMOH+SMV(I)
        IF ((SOMOH-OHPNT)/F.GT.-1.E-3) THEN
          fin=POPUL(1,I-1)+1
          SPCOH=I
          DEBUT=POPUL(1,SPCOH)
          HPACE=-1
        END IF
        IF (RSV(POPUL(1,I)).EQ.OH) THEN
          SOMOH=SOMOH+SMV(I)
          IF ((SOMOH-OHPNT)/F.GT.-1.E-3) THEN
            fin=POPUL(1,I)
            SPCOH=I
            DEBUT=POPUL(1,SPCOH-1)+1
            HPACE=1
          END IF
        END IF
        I=I+1
      END DO

C      RECHERCHE DE L ESPECE NCO
      IF (RSV(1).EQ.SITE) SOMNCO=SOMNCO+SMV(1)
      IF (SOMNCO.GE.NCOPNT) THEN
        LDEBUT=1
        SPCNCO=1
        LFIN=POPUL(1,1)
        PACE=1
      END IF
      IF ((RSV(POPUL(1,1)).EQ.SITE).AND.(SPCNCO.EQ.0)) THEN
        SOMNCO=SOMNCO+SMV(1)
      END IF
      IF (SOMNCO.GE.NCOPNT) THEN
        LDEBUT=POPUL(1,1)
        SPCNCO=1
        LFIN=1
        PACE=-1
      END IF

      I=2
      DO WHILE ((SPCNCO.EQ.0).AND.I.LE.NT)
        IF (RSV(POPUL(1,I-1)+1).EQ.SITE)
+      SOMNCO=SOMNCO+SMV(I)
        IF ((SOMNCO-NCOPNT)/F.GT.-1.E-3) THEN
          LDEBUT=POPUL(1,I-1)+1
          SPCNCO=I
          LFIN=POPUL(1,SPCNCO)
          PACE=1
        END IF
        IF (RSV(POPUL(1,I)).EQ.SITE) THEN
          SOMNCO=SOMNCO+SMV(I)
          IF ((SOMNCO-NCOPNT)/F.GT.-1.E-3) THEN
            LDEBUT=POPUL(1,I)
            SPCNCO=I
            LFIN=POPUL(1,SPCNCO-1)+1
            PACE=-1
          END IF
        END IF
        I=I+1
      END DO
      CHECK=1
      IF (SPCOH.LE.0 .OR. SPCNCO.LE.0) THEN
        CHECK=0
      END IF
      IF ((SPCOH.EQ.SPCNCO).AND.(SMV(SPCOH).LT.2/F)) THEN
        CHECK=0
      END IF

      END DO

C      ICI ON FORME LA NOUVELLE MOLECULE DE SA PARTIE OH
      COUNT=1
      DO I=DEBUT,fin-HPACE,HPACE
        NEWV(COUNT)=RSV(I)
        COUNT=COUNT+1
      END DO
      SOH=COUNT
      NEWV(COUNT)=3

C      PARTIE NCO
      COUNT=COUNT+1

```

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```

DO I=LDEBUT+PACE, LFIN, PACE
  NEWV(COUNT)=RSV(I)
  COUNT=COUNT+1
END DO
COUNT=COUNT-1

```

## C PERFORMING THE REACTION AND ADJUSTING VECTORS

```

SWV(SPCOH)=SWV(SPCOH)-1/F
IF (SWV(SPCOH).LT.1/F) THEN
  IF (SPCOH.LT.SPCNCO) SPCHCO=SPCNCO-1
  CALL REDUCE(FL,NT,SPCOH,SITE,LINK,OH)
END IF
SWV(SPCNCO)=SWV(SPCNCO)-1/F
IF (SWV(SPCNCO).LT.1/F) THEN
  CALL REDUCE(FL,NT,SPCNCO,SITE,LINK,OH)
END IF
LINK(1+OH)=LINK(1+OH)-1/F
LINK(6)=LINK(6)+1/F
LINK(7)=LINK(7)+1/F
IF (SITE.EQ.2) THEN
  LINK(4)=LINK(4)-1/F
ELSE
  LINK(5)=LINK(5)-1/F
END IF

```

## C CALCUL DU POIDS MOLECULAIRE DE LA NOUVELLE ESPECE

```

POIDS=0
DO I=1,COUNT
  IF (NEWV(I).EQ.4 .OR. NEWV(I).GT.6) THEN
    POIDS=MONO*NEWV(I)/4+POIDS
  END IF
  IF (NEWV(I).EQ.5) POIDS=IBODY+POIDS
  IF (NEWV(I).EQ.0H) POIDS=17+POIDS
  IF (NEWV(I).EQ.SITE) POIDS=42+POIDS
  IF (NEWV(I).EQ.3) POIDS=59+POIDS
END DO

```

## C ON CHERCHE L'EXISTENCE DE CE POIDS MOLECULAIRE DANS POPUL

```

INSERT=0
JUMEAU=0
I=1
DO WHILE (I.LT.NT)
  IF ((POIDS.EQ.POPUL(2,I)).AND.(JUMEAU.EQ.0)) JUMEAU=I
  IF (POIDS.LT.POPUL(2,I)) THEN
    INSERT=I
    I=NT
  END IF
  I=I+1
END DO
IF (INSERT.EQ.0) INSERT=NT+1-NISO
CHECK=0

```

## C SI TROUVE

```

IF (JUMEAU.NE.0) THEN
  DO JJ=JUMEAU,INSERT
    IF (((NEWV(1).EQ.RSV(POPUL(1,JJ-1)+1)).AND.(NEWV(COUNT).EQ.
+ RSV(POPUL(1,JJ))) .OR. ((NEWV(1).EQ.RSV(POPUL(1,JJ))) .AND. (NEWV(CO
- UNT).EQ.RSV(POPUL(1,JJ-1)+1))) .AND. (CHECK.EQ.0)) THEN
      CHECK=1
      SWV(JJ)=SWV(JJ)+1/F
    END IF
  END DO
END IF

```

## C NON TROUVE

```

IF (CHECK.EQ.0) THEN
  DO I=FL,POPUL(1,INSERT-1)+1,-1
    RSV(I+COUNT)=RSV(I)
  END DO
  DO I=1,COUNT,1
    RSV(POPUL(1,INSERT-1)+I)=NEWV(I)
  END DO
  DO I=NT,INSERT,-1
    SWV(I+1)=SWV(I)
    POPUL(2,I+1)=POPUL(2,I)
    POPUL(1,I+1)=POPUL(1,I)+COUNT
  END DO
  SWV(INSERT)=1/F
  POPUL(2,INSERT)=POIDS
  POPUL(1,INSERT)=POPUL(1,INSERT-1)+COUNT
  NT=NT+1
  FL=FL+COUNT
END IF

```

X=LNK(6)/MPOLY/2.

CALL MOLECULE(NT,MONO,IBODY,MW,MN,SN,.TRUE.,NISO)

C write(UNIT,\*) SN,50.+50."MCOO=FLOAT(iter)/F,iter

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C FIN DE L'EVENEMENT

```

CALL SetPort(VAL4(ptr1))
CALL EFFACE(70,13,30,10)
frase$=ISTRGS(ITER)
CALL MoveTo(VAL2(70),VAL2(20))
CALL DrawText(frase$,VAL2(0),VAL2(15))
CALL EFFACE(105,73,30,10)
frase$=ISTRGS(NT)
CALL MoveTo(VAL2(105),VAL2(80))
CALL DrawText(frase$,VAL2(0),VAL2(15))
CALL EFFACE(100,88,30,10)
frase$=ISTRGS(FL)
CALL MoveTo(VAL2(100),VAL2(95))
CALL DrawText(frase$,VAL2(0),VAL2(15))

```

```

IF (MOD(X,0.02).LT.1/F/100) THEN
CALL EFFACE(35,28,43,10)
frase$=RSTRGS(MN)
CALL MoveTo(VAL2(35),VAL2(35))
CALL DrawText(frase$,VAL2(0),VAL2(10))
CALL EFFACE(35,43,43,10)
frase$=RSTRGS(MN)
CALL MoveTo(VAL2(35),VAL2(50))
CALL DrawText(frase$,VAL2(0),VAL2(10))
CALL EFFACE(35,58,43,10)
frase$=RSTRGS(X)
CALL MoveTo(VAL2(35),VAL2(65))
CALL DrawText(frase$,VAL2(0),VAL2(5))
CALL PLOTMM(X,MN, SX2,SY2,OLDX(1),OLDY(1),L2,H2,ptr2,409,2)
CALL PLOTMM(X,MN, SX2,SY2,OLDX(2),OLDY(2),L2,H2,ptr2,341,2)
WRITE(UNIT,14) NT,FL,ITER,X,MN,MN,TIME
heure=INT(AINT(TIME/60.))
frase$=ISTRGS(heure)
if(heure.lt.100) frase$='0'//frase$
if(heure.lt.10) frase$='0'//frase$
temps$=frase$(1:3)//':'
heure=JMOD(INT(AINT(TIME)),60)
frase$=ISTRGS(heure)
if(heure.lt.10) frase$='0'//frase$
temps$=temps$(1:4)//frase$(1:2)
heure=INT((TIME-AINT(TIME))*60.)
frase$=ISTRGS(heure)
if(heure.lt.10) frase$='0'//frase$
temps$=temps$(1:6)//':'//frase$
CALL SHOWTIME(temps$,ptr1)

```

END IF

```

IF (MOD(X,0.1).LT.1/F/100) THEN
CALL PLOTDS(NT, SX3,SY3,L3,H3,ptr3)

```

```

IF(IMPRIIME) THEN
C   WRITE(6,*) "ESPECE OH", (NEWV(I),I=1,SOH-1),1
C   WRITE(6,*) "ESPECE NCO", SITE, (NEWV(I),I=SOH+1,COUNT)
C   WRITE(6,*) "NEW MOLECULE", (NEWV(I),I=1,COUNT)
C   WRITE(6,15) 1,POPUL(2,1),SMV(1),(RSV(I),I=1,POPUL(1,1))
C   J=2
C   DO WHILE(J.LE.NT)
C   WRITE(6,15) J,POPUL(2,J),SMV(J),(RSV(I),I=POPUL(1,J-1)+1,POP
C   U(1,J))
C   J=J+1
C   END DO
C   WRITE(12,*) "NT= ",NT," FL= ",FL," X= ",X," ITER= ",ITER
C   DO J=1,NT
C   WRITE(12,16) J,POPUL(2,J),SMV(J)
C   END DO
C   END IF
END IF
ITER=ITER+1
END DO
CALL PLOTDS(NT, SX3,SY3,L3,H3,ptr3)
WRITE(6,*) "TERMINE"
WRITE(UNIT,*) "DISTRIBUTION FINALE"
WRITE(UNIT,15) 1,POPUL(2,1),SMV(1),(RSV(I),I=1,POPUL(1,1))
J=2
DO WHILE(J.LE.NT)
WRITE(UNIT,15) J,POPUL(2,J),SMV(J),(RSV(I),I=POPUL(1,J-1)+1,
POPUL(1,J))
J=J+1
END DO
WRITE(UNIT,*) "LINK WEIGHT VECTOR"
WRITE(UNIT,13) (LINK(I),I=1,7)
CLOSE(11)
CLOSE(12)
WRITE(6,*) "VOULEZ-VOUS IMPRIMER ? (OUI=1,NON=0)"
READ(5,*) IMP
IF(IMP.EQ.1) THEN
CALL GPDump(VAL4(ptr1),VAL4(ptr2),VAL4(ptr3),0)
END IF

```

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```
      PAUSE
10     FORMAT (' ',2X,I5,' ',I6,' ', F6.3)
11     FORMAT (' ',20(I4,1X))
12     FORMAT (' ',10(F7.3, 2X))
13     FORMAT (' ',10(F7.2, 2X))
14     FORMAT (' ',I4,' ',I5,' ',I5,' ',F4.3,' ',F6.0,' ',F6.0,' ',F6.1)
15     FORMAT (' ',2X,I5,4X,I6,4X, F6.3,20(I4,1X))
16     FORMAT (' ',2X,I5,4X,I6,4X, F6.3)
      END
C ***** FIN DU PROGRAMME PRINCIPAL *****
```

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```

C .....
C SOUS-PROGRAMME MODIFIANT LA POLICE D'IMPRESSION
C .....
      SUBROUTINE POLICE(N1,N2,N3)
      integer*4 N1,N2,N3
      CALL TextFont(Val2(N1))
      CALL TextSize(Val2(N2))
      CALL TextFace(Val2(N3))
      END

C .....
C Str255 function
C Make a Pascal string from a FORTRAN string
C .....
      CHARACTER*256 FUNCTION Str255(string)
      CHARACTER*(*) string
      Str255 = CHAR(LEN(TRIM(string)))//string
      RETURN
      END

```

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```

C .....
C SOUS-PROGRAMME CREEANT UNE FENETRE
C .....
      SUBROUTINE ECRAN(m,top,left,bottom,right,title,ptr>window)
      RECORD /Rect/ wrect      ! rectangle defining window
      RECORD /WindowRecord/ window ! storage for window
      INTEGER*4 top,left,bottom,right,ptr,m
      CHARACTER*44 title      ! title string for windows
      CHARACTER*256 Str255    ! fortran to pascal string function
      EXTERNAL Str255         ! defined at end of this file
      wrect.top = top         ! where to put second window
      wrect.left = left
      wrect.bottom = bottom
      wrect.right = right
      ptr = NewWindow(window,wrect,Str255(title),val1(.true.),
      + val2(m),val4(0),val1(.false.),val4(0))
      CALL SelectWindow(VAL4(ptr))
      CALL SetPort(VAL4(ptr))
      RETURN
      END

```

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```

C .....
C SOUS-PROGRAMME CONVERTISSANT UN ENTIER EN CHAINE DE CARACTERES
C .....
      FUNCTION ISTRGS(NOMBRE)
      INTEGER*4 NOMBRE,L
      CHARACTER*15 ISTRGS
      CALL NumToString(VAL4(NOMBRE),ISTRGS)
      IF (NOMBRE.NE.0) THEN
        L=INT(ALOG10(ABS(FLOAT(NOMBRE))))+2
      ELSE
        L=2
      ENDIF
      IF (NOMBRE.LT.0) THEN
        L=L+1
      ENDIF
      ISTRGS=ISTRGS(2:L)
      RETURN
      END

C .....
C SOUS-PROGRAMME CONVERTISSANT UN REEL EN CHAINE DE CARACTERES
C .....
      FUNCTION RSTRGS(NOMBRE)
      CHARACTER*30 RSTRGS,RESTS
      INTEGER*4 ENTIER,L
      REAL*4 NOMBRE
      ENTIER=INT(AINT(NOMBRE))
      CALL NumToString(VAL4(ENTIER),RSTRGS)
      IF (NOMBRE.NE.0.) THEN
        L=INT(ALOG10(ABS(NOMBRE)))+2
      ELSE
        L=2
      ENDIF
      RSTRGS=TRIM(ADJUSTL(RSTRGS))
      ENTIER=ABS(INT((NOMBRE-AINT(NOMBRE))*1000))
      CALL NumToString(VAL4(ENTIER),RESTS)
      DO I=INT(ALOG10(FLOAT(ENTIER))+1),2
        RESTS="0"//RESTS
      END DO
      RSTRGS=RSTRGS(2:L)//CHAR(46)//RESTS(2:4)
      RETURN
      END

```



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```

C *****
C CE SOUS-PROGRAMME GENERE LE FORMAT D'UN GRAPH
C
C W = WINDOW NUMBER
C X1= UPPER left corner pixel x
C Y1= UPPER left corner pixel y
C X2= BOTTOM right corner pixel x
C Y2= BOTTOM right corner pixel y
C XMIN, XMAX, YMIN, YMAX = scale definition
C GRID = 0: No grid, GRID=1, grid lines
C *****
      SUBROUTINE INITPLOT(ptr,X1,Y1,X2,Y2,XMIN,XMAX,YMIN,YMAX,G,SX,SY,
+      largeur,hauteur)
      INTEGER*4 ptr,X1,Y1,X2,Y2,G,largeur,hauteur,ox,oy,XOLD,YOLD
      REAL*4 XMIN,XMAX,YMIN,YMAX,PROPX,PROPY,SX,SY
      CHARACTER*30 NS
      CHARACTER*256 ISTRGS,RSTRGS ! integer/REAL to strings$ function
      CHARACTER*256 Str255 ! fortran to pascal string function
      EXTERNAL Str255,ISTRGS,RSTRGS ! defined at end of this file
      RECORD/Rect/r
      CALL SetPort(VAL4(ptr))
      largeur=X2-X1
      hauteur=Y2-Y1
      PROPX=.8
      PROPY=.8
      SX=PROPX*largeur/(XMAX-XMIN)
      SY=PROPY*hauteur/(YMAX-YMIN)
      ox=NINT((1-PROPX)/2*largeur)
      oy=NINT((1-PROPY)/2*hauteur)
      XOLD=ox
      YOLD=oy
      r.top=oy
      r.left=ox
      r.bottom=oy+NINT(PROPY*hauteur)
      r.right=ox+NINT(PROPX*largeur)
      CALL PenSize(VAL2(2),VAL2(2))
      CALL FrameRect(r)
      CALL PenSize(VAL2(1),VAL2(1))
      CALL POLICE(21,9,0)
      CALL MoveTo(Val2(ox-25),Val2(oy+2))
      NS=ISTRGS(INT(YMAX))
      CALL DrawText(NS,Val2(0),VAL2(INT(ALOG10(YMAX))+1))
      CALL MoveTo(Val2(ox-5),Val2(oy+NINT(PROPY*hauteur)+10))
      NS=ISTRGS(INT(XMIN))
      CALL DrawText(NS,Val2(0),VAL2(INT(ALOG10(XMIN))+1))
      CALL MoveTo(Val2(ox-25),Val2(oy+NINT(PROPY*hauteur)+2))
      NS=ISTRGS(INT(YMIN))
      CALL DrawText(NS,Val2(0),VAL2(INT(ALOG10(YMIN))+5))
      CALL MoveTo(Val2(ox+INT(PROPX*largeur)-70),
+      Val2(oy+NINT(PROPY*hauteur)+10))
      NS=ISTRGS(INT(XMAX))
      CALL DrawText(NS,Val2(0),VAL2(INT(ALOG10(XMAX))-1))
      IF(G.EQ.1) THEN
        I=2
        DO WHILE(I.LE.8)
          CALL MoveTo(Val2(ox),Val2(oy+NINT(PROPY*hauteur/10*I)))
          CALL Line(Val2(INT(PROPX*largeur)-1),Val2(0))
          CALL MoveTo(Val2(ox+NINT(PROPX*largeur/10*I)),Val2(oy))
          CALL Line(Val2(0),Val2(INT(PROPY*hauteur)-1))
          I=I+2
        END DO
      END IF
      CALL MoveTo(Val2(r.left),Val2(r.bottom))
      RETURN
      END

```

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```

C *****
C CE SOUS-PROGRAMME CALCUL MW(N), MN(N) ET LA QTÉ TOTALE (MOLES)
C
C INPUT: NT,MONO,IBODY      OUTPUT: MW,MN,SN
C *****
      SUBROUTINE MOLECULE(NT,MONO,IBODY,MW,MN,SN,CHOIX,NISO)
      logical CHOIX
      integer*2 RSV(60000),NEWV(20000)
      integer*4 POPUL(2,3000)
      integer*4 NT,MONO,IBODY,FIN,NISO
      real*4 SWV(3000),MW,MN,SN,POIDS
      real*8 SNM,SNM2
      COMMON POPUL,RSV,NEWV,SWV
      SNM=0.
      SN=0.
      SNM2=0.
      IF (CHOIX) THEN
        FIN=NT
      ELSE
        FIN=NT-NISO
      END IF
      DO I=1,FIN
        POIDS=FLOAT(POPUL(2,I))
        SNM=POIDS*SWV(I)+SNM
        SN=SWV(I)+SN
        SNM2=POIDS*POIDS*SWV(I)+SNM2
      END DO
      MW=REAL(SNM2/SNM)
      MN=REAL(SNM)/SN
      RETURN
      END

```

4/6/95 10:06 AM

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```

C *****
C CE SOUS-PROGRAMME CALCUL UNE MATRICE COMPRENANT LE POIDS
C MOLECULAIRE DE CHACUNE DES ESPECES ET LEUR POSITION TERMINALE
C DANS LE REACTOR SPACE VECTOR
C *****
      SUBROUTINE POP(FLAG,NT,MONO,IBODY)
      integer*2 RSV(60000),NEWV(20000)
      integer*4 POPUL(2,3000),SPECIE,MN,FLAG
      integer*4 NT,MONO,IBODY,LAST,NOW
      real*4 SWV(3000)
      COMMON POPUL,RSV,NEWV,SWV
      LAST=RSV(1)
      MN=0
      SPECIE=0
      DO I=1,FLAG
        NOW=RSV(I)
        IF (NOW.EQ.4 .OR. NOW.GT.6) MN=MN+MONO*NOW/4
        IF (NOW.EQ.5) MN=MN+IBODY
        IF (NOW.EQ.1.OR. NOW.EQ.0) MN=17+MN
        IF ((NOW.EQ.2).OR.(NOW.EQ.6)) MN=42+MN
        IF (NOW.EQ.3) MN=59+MN
        IF ((LAST.EQ.4 .AND. NOW.LE.1).OR.(LAST.EQ.5 .AND. NOW.EQ.2).OR.
          * (LAST.GT.6 .AND. NOW.LE.1) .OR. (LAST.EQ.5 .AND. NOW.EQ.6)) THEN
          SPECIE=SPECIE+1
          POPUL(1,SPECIE)=I
          POPUL(2,SPECIE)=MN
          MN=0
        END IF
        LAST=NOW
      END DO
      NT=SPECIE
      RETURN
      END

```

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C .....
C CE SOUS-PROGRAMME ÉLIMINE LES ESPECES DONT LA QTÉ PRÉSENTE
C EST INFÉRIEURE À UN 1/F
C .....

SUBROUTINE REDUCE(FLAG,NT,I,SITE,LINK,OH)
integer*2 RSV(60000),NEWV(20000)
integer*4 POPUL(2,3000),NT,FLAG,SHIFT,START,I,FOH,FNCO,SITE,OH
real*4 SMV(3000),AMOUNT,LINK(2)
COMMON POPUL,RSV,NEWV,SMV
FOH=0
FNCO=0
AMOUNT=SMV(I)
SHIFT=POPUL(1,1)
START=1
IF (I.GT.1) THEN
  SHIFT=POPUL(1,I)-POPUL(1,I-1)
  START=POPUL(1,I-1)+1
END IF
IF (RSV(START).LE.1) FOH=1
IF (RSV(POPUL(1,I)).LE.1) FOH=FOH+1
IF (RSV(START).EQ.SITE) FNCO=1
IF (RSV(POPUL(1,I)).EQ.SITE) FNCO=FNCO+1
DO J=I,NT-1
  SMV(J)=SMV(J+1)
  POPUL(1,J)=POPUL(1,J+1)-SHIFT
  POPUL(2,J)=POPUL(2,J+1)
END DO
DO J=START,FLAG-SHIFT
  RSV(J)=RSV(J+SHIFT)
END DO
FLAG=FLAG-SHIFT
NT=NT-1
IF (RSV(START).LE.1) FOH=FOH-1
IF (RSV(POPUL(1,I)).LE.1) FOH=FOH-1
IF (RSV(START).EQ.SITE) FNCO=FNCO-1
IF (RSV(POPUL(1,I)).EQ.SITE) FNCO=FNCO-1
SMV(I)=SMV(I)+AMOUNT
LINK(1+OH)=LINK(1+OH)-(REAL(FOH))*AMOUNT
IF (SITE.EQ.2) THEN
  LINK(4)=LINK(4)-(REAL(FNCO))*AMOUNT
ELSE
  LINK(5)=LINK(5)-(REAL(FNCO))*AMOUNT
END IF
RETURN
END

```

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```

C .....
C CE SOUS-PROGRAMME TRACE LA DISTRIBUTION DE POIDS MOLECULAIRE
C .....

      SUBROUTINE PLOTDS(NT,SX,SY,L,H,ptr)
      integer*2 RSV(60000),NEWV(20000)
      integer*4 POPUL(2,3000),ox,oy,IX,IY
      integer*4 NT,L,H,ptr
      real*4 SMV(3000),SX,SY,LEMAX,classe(50),cat
      RECORD/Rect/r
      COMMON POPUL,RSV,NEWV,SMV
      ox=INT(.1*L)+1
      oy=INT(.1*H)+1
      r.top=oy+2
      r.left=ox+5
      r.bottom=INT(.9*H)-2
      r.right=INT(.9*L)-5
      CALL SetPort(VAL4(ptr))
      CALL EraseRect(r)
      cat=4.477/50.
      DO J=1,50
         classe(J)=0.
      END DO
      DO I=1,NT
         J=INT((ALOG10(FLOAT(POPUL(2,I)))-1.)/cat)
         IF((J.GT.0).AND.(J.LE.50)) classe(J)=classe(J)+SMV(I)
      END DO
      LEMAX=0.
      DO I=1,50
         IF (classe(I).GT.LEMAX) LEMAX=classe(I)
      END DO
      DO I=1,50
         IX=ox+INT((FLOAT(I)*cat)*.8*FLOAT(L)/4.477)
         CALL MoveTo(Val2(IX),Val2(INT(.9*H)-1))
         IY=INT(classe(I)/LEMAX*9.*SY)
         IF (IY.LE.(INT(.8*H))) THEN
            CALL LineTo(Val2(IX),Val2(INT(.9*H)-IY-1))
         END IF
      END DO
      RETURN
      END

C .....
C CE SOUS-PROGRAMME TRACE LE POIDS MOLECULAIRE
C .....

      SUBROUTINE PLOTMM(X,MM,SX,SY,OLDX,OLDY,L,H,ptr,couleur,gros)
      integer*4 ox,oy,IX,IY
      integer*4 L,H,ptr,OLDX,OLDY,couleur,gros
      real*4 X,MM,SX,SY
      ox=INT(.1*L)+1
      oy=INT(.1*H)+1
      CALL SetPort(VAL4(ptr))
      IX=ox+INT(X*SX)
      IY=oy-INT(MM*SY)
      IF (IY.GE.oy) THEN
         CALL ForeColor(Val4(couleur))
         CALL PenSize(VAL2(gros),VAL2(gros))
         CALL MoveTo(Val2(OLDX),Val2(OLDY))
         CALL LineTo(Val2(IX),Val2(IY))
         CALL ForeColor(Val4(30))
      END IF
      OLDX=IX
      OLDY=IY
      CALL PenSize(VAL2(1),VAL2(1))
      RETURN
      END

```

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```

C .....
C  SOUS-PROGRAMME SERVANT A ALIMENTER LE GENERATEUR DE
C  NOMBRE ALÉATOIRE AVEC LA DATE ET L'HEURE DU SYSTEME
C .....
      SUBROUTINE RANDOMIZE()
      INTEGER*4 GETAS
      INLINE(GETAS=z'2e8d')
      Integer*4 sec
      RECORD /QuickdrawGlobals/ QDGlobals
      POINTER (p.QDGlobals, QDGlobals)
      p.QDGlobals = LONG(GETAS()) - SIZEOF(/QuickdrawGlobals/)
      CALL GetDateTime(sec)
      QDGlobals.randSeed = sec
      RETURN
      END

C .....
C  SOUS-PROGRAMME FONCTION RETOURNANT UN NOMBRE ALÉATOIRE
C .....
      FUNCTION RND()
      REAL*4 RND
      RND=(32767.-FLOAT(Random()))/65534.
      RETURN
      END

C .....
C  SOUS-PROGRAMME EFFACANT UNL CHAMP DANS UNE FENETRE
C .....
      SUBROUTINE EFFACE(X,Y,L,H)
      integer*4 X,Y,L,H
      CALL ForeColor(Val4(30))
      CALL PenSize(VAL2(6),VAL2(9))
      CALL MoveTo(Val2(X),Val2(Y))
      CALL LineTo(Val2(X+L),Val2(Y))
      CALL ForeColor(Val4(33))
      RETURN
      END

```

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```

C*****
C      SOUS-PROGRAMME ESTIMANT Mn et Mw selon Macosko
C*****
SUBROUTINE MACOSKO(IBODY,MN1,MCOOH,L2,H2, SX2,SY2,ptr2,NT,NISO,E)
  integer*2 RSV(60000),NEWV(20000)
  integer*4 POPUL(2,3000),NT,NISO,BORNE
  integer*4 IBODY,OLDX(2),OLDY(2),L2,H2,ptr2
  real*4 MN,MN1,MCOOH,X,SX2,SY2,FE,GE,BODY,R
  real*4 MAFAF,MBFBF,SAF,SBF,ma,mb,map,mbp,MAFZAF,MBFZBF
  real*4 GMA,GMB,SWV(3000),E
  COMMON POPUL,RSV,NEWV,SWV
  MAFAF=0.
  MAFZAF=0.
  SAF=0.
  DO I=1,NT-NISO
    MAFAF=MAFAF+POPUL(2,I)*SWV(I)
    MAFZAF=MAFZAF+POPUL(2,I)*POPUL(2,I)*SWV(I)
    SAF=SAF+SWV(I)
  END DO
  MBFBF=0.
  MBFZBF=0.
  SBF=0.
  DO I=NT-NISO+1,NT
    MBFBF=MBFBF+POPUL(2,I)*SWV(I)
    MBFZBF=MBFZBF+POPUL(2,I)*POPUL(2,I)*SWV(I)
    SBF=SBF+SWV(I)
  END DO
  FE=2.
  GE=2.
  ma=MAFAF/SAF/FE
  mb=MBFBF/SBF/GE
  map=MAFZAF/SAF/FE
  mbp=MBFZBF/SBF/GE
  GMA=FE*ma
  GMB=GE*mb
  BODY=FLOAT(IBODY)
  R=1/MCOOH
  MN=(MAFAF+MBFBF)/(SAF+SBF)
  MN1=((1/MCOOH)*MN1+BODY*BODY)/(QMN1/MCOOH+BODY)
  OLDX(1)=INT(.1*L2)+1
  OLDX(2)=OLDX(1)
  OLDY(1)=H2-INT(.1*H2+MN*SY2)-1
  OLDY(2)=H2-INT(.1*H2+MN*SY2)-1
  BORNE=INT(E)
  DO I=1,BORNE,1
    X=FLOAT(I)/100.
    MN=(MAFAF+MBFBF)/(SAF+SBF-FE*X*SAF)
    CALL PLOTMN(X,MN,SX2,SY2,OLDX(2),OLDY(2),L2,H2,ptr2,33,1)
    MN=(R*X*map+X*mbp)/(R*X*ma+X*mb)
    MN1=(X*X*R*(X*(FE-1.)*GMB+GMB-X*R*(GE-1.)*GMA+GMA+2*GMA*GMB)/
    (X*R*ma-X*mb)/(1.-X*X*R*(FE-1.)*(GE-1.))
    CALL PLOTMN(X,MN,SX2,SY2,OLDX(1),OLDY(1),L2,H2,ptr2,33,1)
  END DO
  RETURN
END

```

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```

C.....
C  SOUS-PROGRAMME INITIANT L'HORLOGE VIRTUEL
C.....
      SUBROUTINE INITTIME(ptr)
      integer*4 ptr
      RECORD/Rect/r
      r.top=150
      r.bottom=180
      r.left=15
      r.right=115
      CALL SetPort(VAL4(ptr))
      CALL ForeColor(VAL4(33))
      CALL PenSize(VAL2(2),VAL2(2))
      CALL FrameRect(r)
      CALL ForeColor(VAL4(33))
      r.top=133
      r.bottom=150
      r.left=15
      r.right=115
      CALL FrameRect(r)
      r.top=153
      r.bottom=177
      r.left=18
      r.right=112
      CALL PenSize(VAL2(1),VAL2(1))
      CALL FrameRect(r)
      CALL MoveTo(VAL2(18),VAL2(146))
      CALL POLICE(21,12,0)
      CALL DrawText('VIRTUAL CLOCK',VAL2(0),VAL2(13))
      CALL POLICE(21,9,0)
      RETURN
      END

```

```

C.....
C  THIS SUBROUTINE DISPLAYS THE VIRTUAL TIME INTO WINDOW ptr1
C.....
      SUBROUTINE SHOWTIME(TEMPSS,ptr1)
      integer*4 ptr1
      character*9 TEMPSS
      RECORD/Rect/r
      r.top=154
      r.bottom=176
      r.left=19
      r.right=111
      CALL SetPort(VAL4(ptr1))
      CALL EraseRect(r)
      CALL MoveTo(VAL2(20),VAL2(172))
      CALL POLICE(21,18,1)
      CALL ForeColor(VAL4(205))
      CALL DrawText(TEMPSS,VAL2(0),VAL2(9))
      CALL POLICE(21,9,0)
      RETURN
      END

```

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```

C.....
C      This Subroutine prints (Bitmap) windows 1,2 and 3
C.....
SUBROUTINE GPDump(graPort1,graPort2,graPort3, bitShape)
IMPLICIT NONE
INTEGER*2 errCode
INTEGER*4 graPort1, bitShape, bMapPtr, rectPtr
INTEGER*4 graPort2,graPort3
errCode = 0
CALL PrDrvOpen()
errCode = PrError()
IF (errCode.NE. 0) GOTO 100
CALL PrCtlCall(VAL2(iPrDevCtl),
& VAL4(iPrReset), VAL4(0), VAL4(0) )
errCode = PrError()
IF (errCode.NE. 0) GOTO 100
bMapPtr = LOC(graPort1) + 2 ! bitMap offset
rectPtr = LOC(graPort1) + 16 ! portRect offset
CALL PrCtlCall(VAL2(iPrBitsCtl),
& VAL4(bMapPtr), VAL4(rectPtr), VAL4(bitShape) )
bMapPtr = LOC(graPort2) + 2 ! bitMap offset
rectPtr = LOC(graPort2) + 16 ! portRect offset
CALL PrCtlCall(VAL2(iPrBitsCtl),
& VAL4(bMapPtr), VAL4(rectPtr), VAL4(bitShape) )
bMapPtr = LOC(graPort3) + 2 ! bitMap offset
rectPtr = LOC(graPort3) + 16 ! portRect offset
CALL PrCtlCall(VAL2(iPrBitsCtl),
& VAL4(bMapPtr), VAL4(rectPtr), VAL4(bitShape) )
errCode = PrError()
IF (errCode.NE. 0) GOTO 100
CALL PrCtlCall(VAL2(iPrDevCtl),
& VAL4(iPrPageEnd), VAL4(0), VAL4(0) )
errCode = PrError()
IF (errCode.NE. 0) GOTO 100
CALL PrCtlCall(VAL2(iPrDevCtl),
& VAL4(iPrDocClose), VAL4(0), VAL4(0) )
errCode = PrError()
IF (errCode.NE. 0) GOTO 100
CALL PrDrvClose()
errCode = PrError()
100 continue
RETURN
END

```



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## **APPENDIX B**

**Template for input data file**



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Titre de la simulation	Chaine de caracteres*72
F (tel que masse 1 événement=1/F)	réel
conversion totale	réel
ratio NCOOH	réel
nombre d'isocyanate	entier
nombre de site OH	entier
prop. de l'isocyanate 1	réel
incrément en temps (min)	réel
Réactivité du site NCO #1-OH sec.	10.
Réactivité du site NCO #2-OH sec.	1.
Réactivité du site NCO #1-OH prim.	10.
Réactivité du site NCO #2-OH prim.	1.
Réduction du RSV()	.TRUE. or .FALSE.
Impression à l'écran	.TRUE. or .FALSE.
Prédiction Macosko	.TRUE. or .FALSE.
nombre de classe	entier
MW du monomère	entier
Mw de l'isocyanate	entier
GPC: Mw, qté en mole	entier, réel

.  
.  
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## **APPENDIX C**

### **Example of Screen Output**



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ÉVENEMENT = 18000

MW = 14501.414

MN = 7724.297

X = 0.880

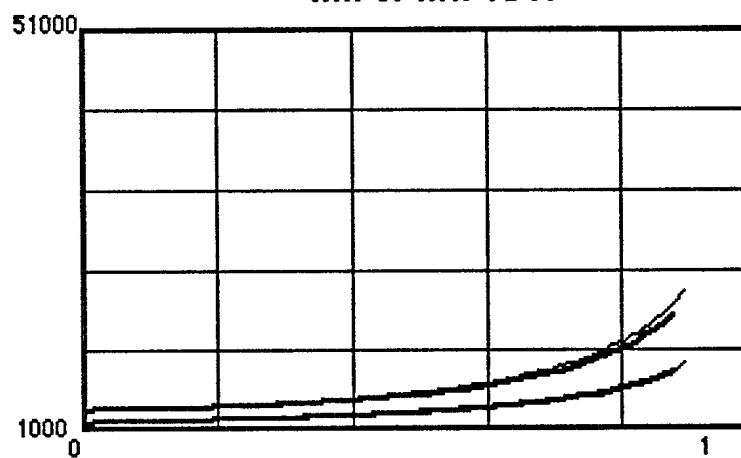
nombre total d'especes: 1297

taille du vecteur RSY: 25619

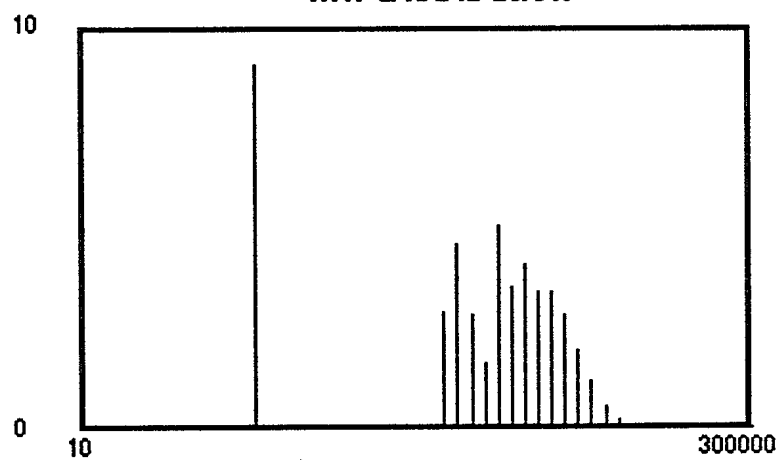
VIRTUAL CLOCK

147:56:00

Mn or Mw vs X



Mw Distribution







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USE OF MONTE-CARLO SIMULATIONS IN POLYURETHANE POLYMERIZATION PROCESSES

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The processing of thermoset energetic polymers involves operations in which a polymerization of initial prepolymer is observed. This chemical reaction brings an important increase of the molecular weight of the polymer. Consequently, the rheological properties of the material are also affected by this curing phenomenon. The extent of this reaction, as well as the type of polymer used, often determine the magnitude of these changes and their effect on the quality of the end-product being processed. In order to optimize the processing window of polyurethane-based formulations, the polymerization reaction has been modeled by Monte-Carlo simulations. For this end, a numerical code has been developed in ANSI Fortran 77 that allows the simulation of  $A_2+B_2$  polymerization with provision for unequal reactivity of the reaction sites. Simulations have been carried out on HTPB-TDI, PPG-HDI and GAP-IPDI systems. A limited experimental validation has confirmed the validity of the molecular weight distributions calculated by the software. The information obtained from these simulations should provide a mean to estimate the material functions of the polymer during the mixing and the casting of a formulation. Minor modifications to the algorithm will enable the simulation of more complex  $A_n+B_n$  systems.

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Monte-Carlo simulations, polymer, polyurethane, stochastic modeling

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